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XLI. *On the Condenser-Telephone.* By G. GREEN, D.Sc.,
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IN 1863, in a letter from Prof. Sir William Thomson † to Professor Tait, there is a reference to the sounds produced by a condenser when charged and discharged. The possibility of constructing a telephone by employing the sheets of a condenser as the vibrating mechanism for transmitting sound was recognized very soon after. Condenser-telephones were made by Varley and by Dolbear about the year 1870, and later by Pollard and Garnier. In the years from 1870 to 1890 numerous attempts were made to produce condenser-telephones which might compete with the electromagnetic telephone. These condenser-telephones were intended for use as ear-phones, and the capacities of the instruments must have been exceedingly small in hand-instruments of this type. This in part explains why the sounds transmitted by them were feeble compared with the sounds transmitted by the ordinary electromagnetic telephones, as we shall see in the discussion to be given later. References are to be obtained to condenser-telephones of the same type at intervals up to the present time, one of the chief instruments described being that by Ort and Rieger in 1907.

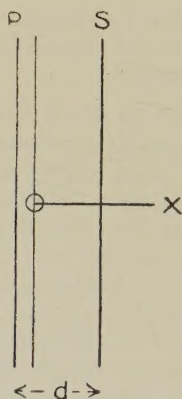
* Communicated by the Author.

† Lord Kelvin's Papers on Electrostatics and Magnetism, § 302.

From some preliminary experiments * which have been made with condensers of a larger type it appeared that the condenser could be made an instrument for transmitting sound of great efficiency as well as one of exceedingly high quality, and the author was induced to carry the investigation further. In the present paper it is proposed to give a preliminary discussion of the mathematical theory of the condenser-telephone when used either as a receiver or as a transmitter. The condenser-telephone transmitter has been in use now for a considerable time, but I am not aware of any complete mathematical discussion of the transmitter applicable to the type of condensers employed in the experiments.

We take first the case of the condenser-telephone receiver. The essential feature required in the condenser is that its

Fig. 1.



plates should be so mounted as to be free to vibrate, and this condition can be fulfilled whether the bounding edges of the plates be free or fixed. There is thus a large number of special cases to be considered depending upon the nature of the elastic restoring force acting upon each plate when disturbed from its equilibrium position. We wish, however, at first simply to investigate the main qualities and possibilities of the condenser as an instrument for reproducing sound and speech, and to indicate the theory used as a guide throughout the experimental investigations. For our present purpose it is sufficient to take the case of a condenser consisting of two metal sheets P and S, having a uniform sheet

* During the early part of the experimental work connected with this investigation I had valuable assistance from Alexander J. Younger, M.A., B.Sc., of this Department.

of dielectric material completely occupying the interspace between them. One of the metal sheets, S, may be regarded as fixed in position in a vertical plane, with the dielectric sheet just in contact with both metal plates, but not exerting any force upon either of them, when the condenser is uncharged. In any actual condenser separate sheets of material of the type considered would not have perfect contact one with the other, and part of the interspace between the plates would always be occupied by air, even when the sheets are laid horizontally and put under pressure. Thus the force acting upon the plate P when disturbed from its equilibrium position would not be wholly due to the elastic resistance of the dielectric material interposed between the metallic plates but in part to the resistance to compression of the layer of air included with the dielectric material. The dielectric may of course be air alone. Nevertheless, for the sake of simplicity in what follows we shall treat the material in the interspace as acting when under pressure like an elastic medium having a Young's Modulus Y.

When the condenser is charged, the metal plates attract each other and the dielectric is compressed by an amount depending upon the charge upon each plate. If d be the original distance apart of the plates, and a the amount the plate P moves towards plate S due to a fixed charge Q_0 , we have

$$YA \frac{a}{d} = \frac{2\pi Q_0^2}{Ak}, \dots \dots \dots (1)$$

A being the area of each plate, and k being the specific inductive capacity of the dielectric. Let now the position of plate P when Q_0 is the charge upon each plate be taken as origin, and let x denote the distance of plate P from the origin at any later time, x being positive for a motion of plate P towards plate S. Assuming now that the total charge on each plate at any instant Q is represented by $Q = Q_0 + q$, where q is a small quantity of the type $b \sin(\omega t + e)$, we have to determine the corresponding motion of the plate P. This motion will be resolvable into a series of simple harmonic motions about a mean position, each of which motions is communicated to the air on the open side of the plate P. It is easy to show that the force applied by the air in contact with the plate is equivalent to a resisting force which can be represented by $\kappa \dot{x}$, where κ is a constant which we shall determine later from hydrodynamical considerations. The equation of motion of plate P can now be

written in the form

$$m\ddot{x} + \kappa\dot{x} + YA \frac{a+x}{d} - \frac{2\pi Q^2}{Ak} = 0, \quad \dots \quad (2)$$

where m is the total mass of the plate. As we employ electromagnetic units below, we now replace Q by Qv , where v is the velocity of light. In virtue of equation (1) the above may be written in the form

$$m\ddot{x} + \kappa\dot{x} + YA \frac{x}{d} - \frac{4\pi Q_0 v^2}{Ak} q - \frac{2\pi v^2}{Ak} q^2 = 0, \quad \dots \quad (3)$$

q being a quantity which remains to be determined by consideration of the electrical conditions obtaining in the condenser circuit.

A typical condenser-telephone circuit would consist of a condenser, whose capacity when the plate P is at the origin we may represent by C_0 , a transformer secondary coil of inductance L in series with the condenser, and a battery of e.m.f. E , the total resistance of the circuit being represented by R . If we assume that a small variable e.m.f. $e \sin \omega t$ is applied to this circuit by means of the transformer, the equation determining the total charge Q at any instant on each condenser plate is given by

$$L \frac{d^2 Q}{dt^2} + R \frac{dQ}{dt} + \frac{Q}{C} = E + e \sin \omega t \quad \dots \quad (4)$$

If we take $Q_0 = C_0 E$, the charge on each plate produced by the battery e.m.f. E acting alone, we have $Q = Q_0 + q$ and q is determined by

$$L \frac{d^2 q}{dt^2} + R \frac{dq}{dt} + \frac{Q_0 + q}{C} - \frac{Q_0}{C_0} = e \sin \omega t. \quad \dots \quad (5)$$

At any instant t , the moving plate P is in the position x , and the capacity of the condenser is then given by

$$C = \frac{Ak}{4\pi(d-a-x)v^2} = C_0 \left(1 + \frac{x}{d-a}\right),$$

so that the equation to determine q is finally obtained in the form

$$L \frac{d^2 q}{dt^2} + R \frac{dq}{dt} + \frac{q}{C_0} = e \sin \omega t + \frac{E}{d-a} x. \quad \dots \quad (6)$$

We may assume that x can be represented by

$$x = X \sin(\omega t + \epsilon),$$

and the solution of this equation can then be written down as

$$q = \alpha \left\{ e \sin \omega t + \frac{EX}{d-a} \sin (\omega t + \epsilon) \right\} - \beta \left\{ e \cos \omega t + \frac{EX}{d-a} \cos (\omega t + \epsilon) \right\},$$

where

$$\alpha = \frac{C_0(1 - LC_0\omega^2)}{\{(1 - LC_0\omega^2)^2 + R^2C_0^2\omega^2\}} = \frac{C_0 \cos \theta}{\sqrt{\{(1 - LC_0\omega^2)^2 + R^2C_0^2\omega^2\}}},$$

$$\beta = \frac{RC_0^2\omega}{\{(1 - LC_0\omega^2)^2 + R^2C_0^2\omega^2\}} = \frac{C_0 \sin \theta}{\sqrt{\{(1 - LC_0\omega^2)^2 + R^2C_0^2\omega^2\}}},$$

and

$$\tan \theta = \frac{RC_0\omega}{(1 - LC_0\omega^2)}. \quad \dots \quad (7)$$

The value of q is accordingly obtained as

$$q = \frac{eC_0 \sin (\omega t - \theta)}{\sqrt{\{(1 - LC_0\omega^2)^2 + R^2C_0^2\omega^2\}}} + \frac{\alpha E}{(d-a)} x - \frac{\beta E}{\omega(d-a)} \dot{x}, \quad (8)$$

and we have to insert this value of q in equation (3) above, and determine the corresponding value of x .

As we have assumed that q is a small quantity of the first order of smallness compared with Q_0 , we at present omit the term $\frac{2\pi v^2}{Ak} q^2$ in equation (3). When we insert the value of q given above, and replace $\frac{4\pi Q_0 v^2}{Ak}$ by $\frac{E}{d-a}$, this equation becomes

$$\ddot{x} + K\dot{x} + n^2x = B \sin (\omega t - \theta),$$

where

$$K = \left[\frac{\kappa}{m} + \frac{E^2 C_0 \sin \theta}{\omega m (d-a)^2 \sqrt{\{(1 - LC_0\omega^2)^2 + R^2 C_0^2 \omega^2\}}} \right],$$

$$n^2 = \left[\frac{YA}{md} - \frac{E^2 C_0 \cos \theta}{m (d-a)^2 \sqrt{\{(1 - LC_0\omega^2)^2 + R^2 C_0^2 \omega^2\}}} \right],$$

$$B = \frac{eEC_0}{m(d-a) \sqrt{\{(1 - LC_0\omega^2)^2 + R^2 C_0^2 \omega^2\}}}. \quad \dots \quad (9)$$

The solution of equation (9) takes the well-known form

$$x = \frac{B}{\sqrt{\{(n^2 - \omega^2)^2 + K^2 \omega^2\}}} \sin (\omega t - \theta - \phi); \quad \tan \phi = \frac{K\omega}{(n^2 - \omega^2)} \quad \dots \quad (10)$$

for the case where n^2 is a positive quantity. We are

concerned chiefly with the amplitude of the motion of the plate P, which is accordingly represented by

$$\text{amp.} = \frac{eEC_0}{m(d-a)\sqrt{\{(1-LC_0\omega^2)^2 + R^2C_0^2\omega^2\} \{(n^2-\omega^2)^2 + K^2\omega^2\}}} \dots (11)$$

The above solution applies to the most important case in practice of the use of a condenser as a receiver, namely, that in which a considerable steady voltage is applied to the condenser plates in addition to the varying voltages applied through the action of the transformer coil in transmitting electrical vibrations from the primary to the condenser circuit. The corresponding results for the case where $E=0$ and where the term $\frac{2\pi q^2}{Ak}$ is retained, can readily be obtained from the equations given above.

Before entering into the discussion of the above solution it is convenient to derive the corresponding solution for the case of a condenser used as a transmitter. In this case we assume that an external force represented by $M \sin \omega t$ is applied to the plate P of the condenser, and the problem is to determine the amplitude of the electrical vibrations thereby produced in the condenser circuit, and transmitted to a secondary circuit by the transformer. Instead of the equation of motion of plate P given by (3) above, we have now

$$m\ddot{x} + \kappa\dot{x} + YA \frac{x}{d} - \frac{4\pi Q_0}{Ak} v^2 q - \frac{2\pi}{Ak} v^2 q^2 = M \sin \omega t. \quad (12)$$

Instead of the circuit equation given by (6) above, we have now

$$L \frac{d^2 q}{dt^2} + R \frac{dq}{dt} + \frac{q}{C_0} = \frac{E}{(d-a)} x, \dots (13)$$

so that the value of q the variable part of the condenser charge is again given by equation (8) with e equal to zero. The equation to determine x corresponding to equation (9) above is

$$\ddot{x} + K\dot{x} + n^2 x = \frac{M}{m} \sin \omega t, \dots (14)$$

where K and n^2 have the values indicated in equation (9).

The solution of (14) gives x the displacement of plate P at time t in the form

$$x = \frac{M}{m \sqrt{\{(n^2-\omega^2)^2 + K^2\omega^2\}}} \sin(\omega t - \phi); \quad \tan \phi = \frac{K\omega}{(n^2-\omega^2)}, \dots (15)$$

and the variable charge on the condenser, q , arising from the application of the external force $M \sin \omega t$ is represented by

$$q = \frac{MEC_0 \sin (\omega t - \phi - \theta)}{m(d-a) \sqrt{\{(1-LC_0\omega^2)^2 + R^2C_0^2\omega^2\} \{ (n^2 - \omega^2)^2 + K^2\omega^2 \}}}. \quad (16)$$

From this the value of the current in the condenser circuit can be readily derived, if required. The corresponding solution for the case where $E=0$ can be worked out from the above equations, but it is not of so much value in practice.

The main results with which we are concerned are contained in equations (9), (11), and (16). These equations show that the best conditions of working of a condenser-telephone either as a receiver or as a transmitter depend upon the values chosen for the frequency of mechanical vibration represented by $\frac{n}{2\pi}$, and for the frequency of electrical vibration of the condenser circuit represented by the value of $\frac{\omega}{2\pi}$ which makes $\{(1-LC_0\omega^2)^2 + R^2C_0^2\omega^2\}$ a minimum. In what follows we shall confine our attention to the case of the receiver as indicated by equations (9) and (11), as it is easy to derive the corresponding results for the transmitter from equations (15) and (16).

We may regard $\frac{\omega_0}{2\pi}$ as the natural frequency of the condenser circuit, where $LC_0\omega_0^2=1$. If the vibrations imposed upon the condenser circuit are of frequency $\frac{\omega_0}{2\pi}$, we have electrical resonance and $\cos \theta$ is then zero. The frequency of vibration of the condenser plate is then given by

$$\frac{n}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{YA}{md}},$$

in which Y is a constant depending upon the elastic resistance of the dielectric material to compression and upon the resistance to compression of the air imprisoned between the plates of the condenser. As the values of Y have not yet been obtained experimentally, we may estimate that a lower limit for its value would be obtained by taking the dielectric to be air completely imprisoned between the plates.

This gives $Y = \gamma\pi$, where π is atmospheric pressure, or $Y = 1.42 \times 10^6$ dynes per square centimetre. In a condenser composed of tinfoil sheets of mass .005 gram per sq. cm. set so as to be .003 cm. apart, n^2 is of the order 9×10^{10} . When the condition for electrical resonance is not fulfilled, the term in $\cos \theta$ must be included in evaluating n^2 . As the frequency of the imposed vibrations rises above resonance frequency, the value of n^2 increases, and as the frequency of the imposed vibrations falls below resonance frequency the value of n^2 decreases. In this way the mechanical frequency of the condenser plate tends to accommodate itself to suit a wide range of frequency in the vibrations imposed upon the condenser, so that it is impossible for any sharp resonance conditions to exist at any given frequency of the applied vibrations. The electrical frequency of the condenser circuit can be made to agree with the frequency of the most powerful tones of the human voice without any of the usual effects of resonance being evident*.

Consider now the resistance coefficient K . Of the total resistance to the motion of the condenser plate at any instant $mK\dot{x}$, the part $\kappa\dot{x}$ represents the force communicated by the moving plate to the air in contact with it. The motion communicated to the air in the problem which we have been considering consists of a progressive train of waves which may be represented by a velocity-potential $\phi = a \cos \{\omega(x - Vt)\}$, where V indicates the velocity of sound in air. From this we can easily obtain the velocity of an air particle as $-\omega a \sin \{\omega(x - Vt)\}$, and the pressure increase per unit area at plane x by $-\dot{\omega}\rho_0 V a \sin \{\omega(x - Vt)\}$, where ρ_0 is the density of undisturbed air. Thus the force acting on any plane of area A at x is $A\rho_0 V \dot{x}$ and the value of the coefficient $\frac{\kappa}{m}$ is therefore $\frac{A\rho_0 V}{m}$, which is equivalent to $\frac{4.2 A}{m}$. This can be increased by diminishing the mass per unit area of the plates. The remaining part of the coefficient K represented by the term containing $\sin \theta$ has clearly a maximum value at the frequency $\frac{\omega_0}{2\pi} = \frac{1}{2\pi \sqrt{LC_0}}$ which is the frequency at which there is electrical resonance. The value of the term containing $\sin \theta$ in the coefficient K rapidly falls off as the frequency passes away from the value

* See "Analysis of Energy Distribution in Speech," by Crandall & McKenzie, *Physical Review*, xix., 1922.

$\frac{\omega_0}{2\pi}$ corresponding to the condition of electrical resonance.

At very high frequencies the term in $\sin \theta$ is zero, and practically all damping of the motion of the plate is then due to the communication of sound vibrations to the air.

At frequencies below the resonance frequency $\frac{\omega_0}{2\pi}$, the term in $\sin \theta$ diminishes as ω diminishes, rapidly at first and then gradually, reaching the constant value $\frac{E_2 R C_0^2}{m(d-a)^2}$ when $\omega = 0$.

The damping coefficient accordingly varies with the frequency of the imposed vibrations, and is of importance over the whole range of frequency with which we are chiefly concerned in reproducing the human voice. It is to be noted, however, that the variation of the coefficient of resistance is favourable to the formation of a curve of amplitude against frequency which is exceedingly uniform over the range of frequency referred to above as the resistance falls off as the frequency of the applied vibrations passes away from the resonance value on either side.

Consider now the manner in which the amplitude term B of equation (9) varies with the capacity of the condenser, for all values of ω , subject to the condition that the frequency of the circuit $\frac{\omega_0}{2\pi} = \frac{1}{2\pi \sqrt{LC_0}}$ has a certain value

assigned to it. When ω^2 is exceedingly large, B is proportional to C_0 . When $\omega^2 = \frac{1}{LC_0}$, which corresponds with the condition of resonance, B is proportional to $\frac{1}{R\omega_0}$. When

ω^2 is less than ω_0^2 and is tending toward the value zero, B tends to become proportional to C_0 . Thus when the frequency of the imposed vibrations is in the neighbourhood of the frequency of the condenser circuit, the amplitude of the motion of the condenser plate is independent of the value of the capacity of the condenser C_0 . When, however, the imposed vibrations are of low frequency, the amplitude of the motion of the condenser plate depends directly on the value of the capacity of the condenser. This then is the explanation why the early condenser-telephones could only respond feebly to the human voice, for the capacities of the condensers used were exceedingly small and the lower and more important frequencies in the sound issuing from the condenser plates correspondingly weak. In the case of

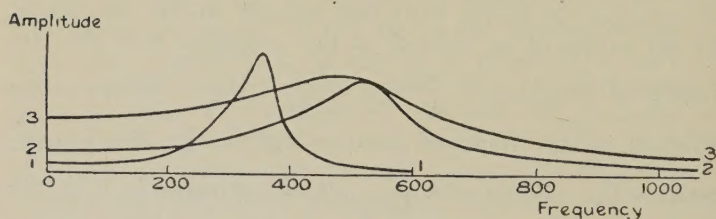
the receiver and also of the transmitter, the value of the capacity of the condenser C_0 must be properly chosen to keep the correct relation between the low and high frequency sounds of the transmitted speech. When the value of the

frequency of the condenser circuit, $\frac{\omega_0}{2\pi} = \frac{1}{2\pi \sqrt{LC_0}}$, is

already fixed for a given type of condenser, the determination of the most suitable value to use for the capacity of the condenser is a matter for experiment. With C_0 very small low frequency sounds are feebly reproduced, and with C_0 very large the low frequency sounds may be too strongly reproduced, as compared with sounds of high frequency.

If a curve be drawn to show the relation between amplitude and frequency as indicated by equation (11), the curve would in general have two maxima corresponding approximately with the value of ω given by $\omega^2 = \frac{1}{LC}$ and $\omega^2 = n^2$ respectively. These two values or frequencies giving a

Fig. 2.



maximum value to the amplitude can be made to coincide so as to give a single maximum of increased value. The two values of ω^2 referred to should be chosen if possible within the range of frequency which is of greatest importance in relation to the frequencies contained in ordinary speech, so as to make the amplitude curve as nearly as possible a uniform straight line over the important range of frequency. Examples of the curves of amplitude and frequency given by equation (11) are shown in fig. 2 for the frequency range 0 to 1000. These curves show only one

maximum corresponding to $\omega^2 = \frac{1}{LC_0}$, the maximum corresponding to $\omega^2 = n^2$ being much beyond frequency 1000 for condensers with air as dielectric to which the curves

refer. The curve marked 1 1 corresponds to the conditions

$$\frac{\omega_0}{2\pi} = 356, \quad \frac{m}{A} = \cdot 005 \text{ grm.}, \quad C_0 = \cdot 2 \text{ mf.},$$

$$E = 150 \text{ volts}, \quad R = 200 \text{ ohms},$$

and the maximum ordinate of the curve represents a displacement of $\frac{7eE \cdot 10^{-26}}{m(d-a)}$ cms. The curves marked 2 2 and

3 3 are for condensers made of the same material, and having the same voltage applied to the plates, but the frequency of the condenser circuit is now 534 instead of 356. These curves show the effect of increase of capacity on the form of the amplitude curve, at a given frequency of the condenser circuit. The curve 2 2 corresponds to a capacity of $\cdot 4$ microfarad and the curve 3 3 to a capacity of 1 microfarad. When the capacity is very small the amplitude curve has a fairly sharp maximum at resonance frequency. When

C_0 is increased up to the value determined by $C_0 = \frac{1}{R\omega_0}$ the

amplitude curve becomes practically a uniform straight line parallel to the frequency axis for the range of frequency

from zero to beyond the value $\frac{\omega_0}{2\pi}$, which can of course be

chosen to include any desired range of frequency. Increase

in amplitude can be obtained by increasing the value of $\frac{m}{A}$,

thus bringing down the frequency corresponding to $\omega^2 = n^2$ nearer to the frequencies of ordinary speech.

The average amount of energy communicated to the air at any given frequency per unit of time, by a vibrating plate of area A , can be found from the expression $\frac{1}{2}\rho_0 V \omega^2 A \times (\text{amplitude})^2$. The sound emitted by a condenser accordingly depends directly on the area of the plate, and the advantage to be obtained by using condensers of large area and therefore large capacity becomes still more apparent than before. The theory which we have been discussing obviously applies with certain modifications to the case of a condenser consisting of a pile of alternately positive and negative plates. In this case the uppermost plate may be regarded as having a displacement approximately n times the displacement of a single plate relative to its nearest neighbour, where n is the total number of plates assumed large. The above expression shows that the energy communicated

to the air by a pile of plates n in number would be n^2 times the amount of energy communicated by a single plate of the same area: and much more energy would be delivered to the air by a condenser of given capacity if its plates were arranged to form a pile than when the condenser consists of only two parallel plates.

The above preliminary discussion of the properties of the condenser-telephone seems to indicate that the instrument has, when properly designed, the most important quality required in a telephone, namely, that of reproducing the vibrations delivered to it uniformly and equally over a very great range of frequency. On the other hand, condenser-telephones of low capacity show decided resonance effects and may be used in bridge-measurements or in heterodyne reception of continuous waves. The results contained in equations (11) and (16) have been verified generally for a considerable range of values of capacity and of voltage, but the experimental verification is still incomplete. The high quality of the reproduction of speech and music by the condenser-telephone has also been amply demonstrated by the experiments which are in progress, and of which I hope to give an account later. Condenser-telephones have also been tested for nearly two years in their use as Loud-Speakers for wireless reception with very satisfactory results. The author hopes to continue the mathematical and experimental investigation of the condenser-telephone, and of questions relating to the condenser circuit, in a later paper.

I wish to take this opportunity of acknowledging my indebtedness to Messrs. Britains Ltd., Cheddleton Paper Mills, near Leek, Staffordshire, who have very kindly provided me with material for the experimental investigation.

XLII. *Note on the High Frequency Oscillatory Discharge in Rarefied Gas.* By R. C. RICHARDS, M.Sc.*

[Plate VIII.]

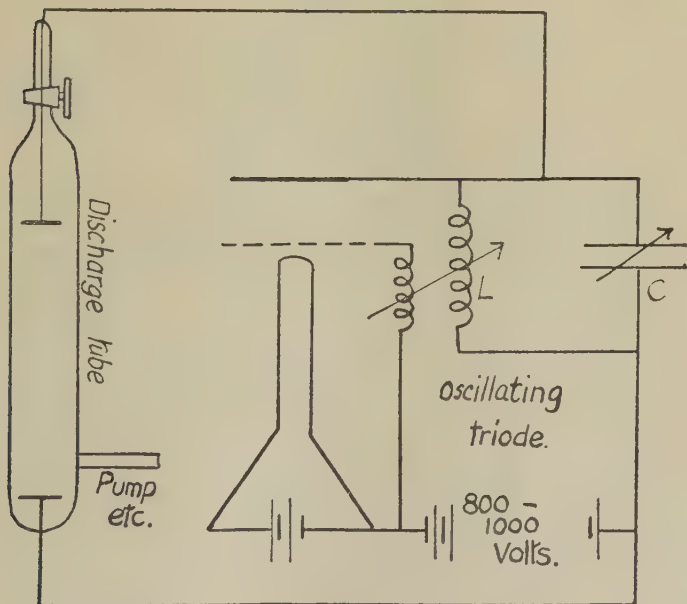
THE familiar experiments which can be carried out by passing a high-tension discharge through rarefied gases are too well known to need any description, and it occurred to the writer to try the effect of a high-tension discharge, of an alternating character, of high frequency.

* Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

The thermionic valve provided a ready source of high frequency oscillatory potential, which can be applied to the discharge-tube in the usual way. The diagram indicates the general method of connexion.

The power valve is provided with an inductance and capacity (LC) in the plate circuit, in series with a steady source of high potential of about 1000 volts, produced by a battery of small accumulators. The grid circuit consists of a reaction coil which can be so coupled to the inductance in the plate circuit as to set up powerful undamped oscillations

Fig. 1

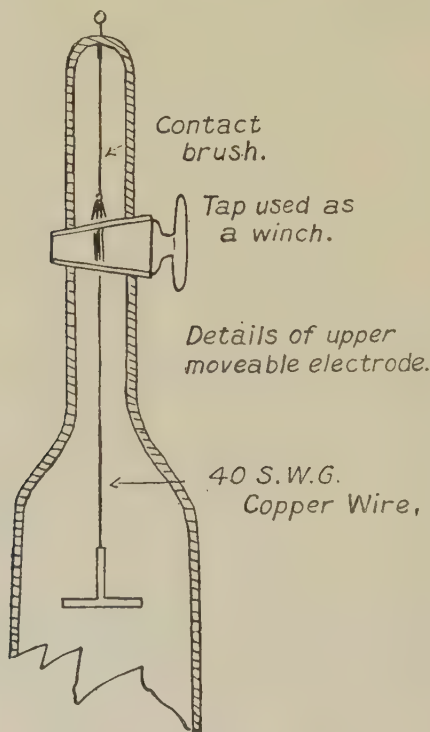


in the plate circuit (LC), their frequency being given approximately by the formula $1/2\pi \sqrt{LC}$. The oscillating circuit is connected to the electrodes of the discharge-tube, and when this latter is exhausted to a sufficient degree, luminous discharge takes place.

A special form of discharge-tube was used, with one fixed and one movable electrode. Thus the distance between the electrodes could be varied. The tube was used in a vertical position, the bottom electrode being fixed. At the top end of the tube an ordinary tap was sealed, the tap barrel having a groove filed in it carrying a thin copper wire from which

was suspended the moving electrode. Thus the tap acted as a winch, winding up the wire and drawing up the electrode, or *vice versa*, a device due originally to Aston. Contact was made through the top of the tube remote from the discharge-tube, by means of a brush, touching the wire coiled on the tap barrel (fig. 2).

Fig. 2.



The appearance of the luminous discharge is characterized by its symmetry, having the same features as the ordinary direct discharges, in its relation to the pressure of the residual gas.

Both electrodes appear to be cathodes, having the usual negative glow and dark spaces, the positive column occupying the central region of the tube, if the electrodes are far enough apart. If they are relatively close together, the appearance of the discharge is that given by photograph I. (Pl. VIII). For relatively high pressures, separating the electrodes will cause the appearance of the continuous positive column.

The most interesting effects are obtained by having the pressure so adjusted as to give a striated positive column. Photograph II. shows the appearance of the tube when the electrodes are so far apart that the striated column is just appearing. It is seen that the striation is "double," consisting as it were of two striations placed back to back.

Hydrogen was the gas used in the tube, and the colour of this double striation was striking, having a pink edge to the usual blue colour of the hydrogen striation. Further separation of the electrodes produces more of these double striations, which seem to grow from the central pair as the electrodes are separated (photograph III.).

Photograph IV. shows the tube with the electrodes widely separated, and a whole series of double striations in the central column, the discharge about the electrodes being still characteristic of a cathode.

If the hand is placed near one end of the tube, the effect is altered considerably, indicating what a large effect the charges on the walls of the tube have on these discharge phenomena.

Photograph V. shows the appearance of the tube, with the hand placed near one end. It appears to cause a slight rectifying effect, for the luminosity round the electrode near the hand is very much diminished, and the striations have completely lost their double appearance.

Speculation on the nature of the double striation is rendered difficult, in the absence of any really decisive information as to the nature of the more frequently observed single striations. There is no doubt that they are of the same nature as these latter, and we may infer that one set belongs to the discharge when passing in one direction, and the other set is generated by the corresponding inverse discharge, the sharp convex surfaces being turned towards the corresponding cathode. The distance between the two members of the double striations can probably be regarded as the distance travelled by the positive ions in the tube during a half-period of the discharge, the frequency of which was of the order of 10^5 .

The experiment described here is of a purely qualitative nature, but it opens up anew the question of the nature of the striated discharge, and further experiments on this point are now in progress.

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University College, London.

XLIII. *On the Theory of the Absorption of X-Rays.* By
Dr. R. A. HOUSTOUN, *Lecturer on Physical Optics in the
University of Glasgow* *.

Introduction.

IT is possible, on the basis of the usual theory of dispersion, to calculate the number of electrons per molecule concerned in the production of an absorption band, such as the absorption bands in the spectra of the aniline colouring matters. I made this calculation in 1909 †, and found that these absorption bands were produced by one electron in each molecule and that the theory seemed to apply well in this case. When the formula was applied to inorganic salts such as cobalt chloride, the result suggested that in this case the vibrating systems were ions, though potassium permanganate was difficult to place. In 1919 ‡ I applied the same theory to the characteristic absorption of X-rays in nine elements, and found that there was one electron per atom concerned in the K absorption, and more—the results varied from two to four—concerned in the production of the L absorption. A. H. Compton § has since made calculations on the same lines. There is considerable doubt in the minds of many workers as to whether the ordinary theory, or, as it is sometimes called, the classical theory, can be applied to the absorption of X-rays, and as we have now additional data available, and I have arrived at a clearer understanding of the points involved, I desire to return to the subject here.

Proof of Formula.—Let a plane wave be passing through an absorbing medium. Let $I d\nu$ be the energy contained within the range of frequency (reciprocal of the period) $d\nu$, which passes through one square centimetre per second, and let

$$e^{-\mu z}$$

represent the rate of diminution of the intensity of the wave. μ is termed the “absorption coefficient.”

The energy received on a parallel plate distant dz from the first one is

$$I d\nu e^{-\mu dz},$$

* Communicated by the Author.

† “On the Mechanism of the Absorption-Spectra of Solutions,” *Proc. Roy. Soc. A*, lxxxi. p. 606 (1909).

‡ “The Absorption of X-Rays,” *Proc. Roy. Soc. Edin.* xl. p. 34 (1919).

§ “Secondary Radiations produced by X-Rays,” *Bulletin of the National Research Council*, 1922.

and the energy absorbed in the layer of 1 sq. cm. surface and thickness dz is

$$I d\nu(1 - e^{-\mu dz}) = I d\nu \mu dz.$$

Let N be the number of molecules per cubic centimetre. Then the number of molecules in the layer is $N dz$ and the amount of energy absorbed per molecule is

$$\frac{\mu I d\nu}{N} \dots \dots \dots (1)$$

§ Let us suppose that in the medium there are a number of electrons which execute vibrations about their mean positions under the influence of the wave. Then the motion of a typical electron may be represented by

$$m \frac{d^2 x}{dt^2} + h \frac{dx}{dt} + f x = -e X, \dots \dots \dots (2)$$

where m is the mass of the electron and X the electric intensity in the wave. The second and third terms represent the frictional resistance and the "quasi-elastic" force. Now the absorption of energy by the electron can be treated in two different ways. We may assume that the free vibration has died down, and that each of the Fourier components into which X can be resolved produces its own forced vibration. Consequently the electron never gains energy; it is being taken away from it as fast as it receives it. This is the usual method of the theory of dispersion, and it leaves the nature of the friction term a mystery.

On the other hand, we may suppose that there is no friction term, that initially the displacement and velocity of the electron are each zero, and that its kinetic energy gradually increases under the influence of the light-wave. Then there is a collision or atomic change that reduces its energy to zero, and the process starts over again. In this way the energy is removed from the electron discontinuously, not continuously. Strange to say, when the intensity I of the wave is given, the expression for the energy absorbed comes out the same on both assumptions.

§ It is not necessary to perform the calculation in the second case, for a similar calculation has already been performed by Planck, and our result can be obtained from his. Planck shows* that the energy absorbed by an oscillator

* 'Vorlesungen über die Theorie der Wärmestrahlung,' §§ 148-9.

per second is

$$\frac{\mathfrak{I}}{4L},$$

where L corresponds to m/e^2 and $\mathfrak{I}$ is defined by

$$\overline{X^2} = \int_0^\infty \mathfrak{I} d\nu,$$

(cf. eqn. 2). The whole energy received per unit area is

$$\int_0^\infty I d\nu = \frac{c\overline{X^2}}{4\pi},$$

where c is the velocity of light. Consequently

$$I = \frac{c}{4\pi} \mathfrak{I},$$

and the energy absorbed per electron per second is

$$\frac{\mathfrak{I}}{4L} = \frac{\pi e^2 I}{mc}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let us suppose that there are p electrons per atom concerned in the absorption. Then from (3) and (1)

$$p = \frac{mc}{\pi e^2 N} \mu d\nu \quad \text{or} \quad p = \frac{mc}{\pi e^2 N} \int \mu d\nu, \quad . \quad . \quad (4)$$

if we integrate over the whole absorption band. We have tacitly assumed that e is measured in electrostatic units.

§ If we retain the friction term in (2) and assume forced vibrations, and $X = A \cos 2\pi\nu t$, we find

$$x = \frac{-Ae \cos(2\pi\nu t - \tan^{-1} 2\pi\nu h/(f - 4\pi^2\nu^2 m))}{((f - 4\pi^2\nu^2 m)^2 + 4\pi^2\nu^2 h^2)^{\frac{1}{2}}}.$$

The rate at which work is being done on the electron is

$$-Xe \frac{dx}{dt}.$$

If we substitute in this expression for X and dx/dt , and take the average value, we obtain

$$\frac{A^2 2\pi^2 \nu^2 e^2 h}{(f - 4\pi^2 \nu^2 m)^2 + 4\pi^2 \nu^2 h^2}$$

Let us assume now that ν varies and graph the above expression as a function of ν . It will be found that the curve falls away rapidly on both sides of a maximum, the position of which we shall denote by ν_m , and that the only

term of importance is the first one in the denominator. We may therefore substitute ν_m for ν in the other term in the denominator and for one of the ν 's in the numerator. Multiply by $d\nu$ and integrate in order to find the energy absorbed from all the Fourier components of the original wave. Then we obtain

$$\int_0^\infty \frac{2A^2\pi^2\nu\nu_me^2h d\nu}{(f-4\pi^2\nu^2m)^2+4\pi^2\nu_m^2h^2} = \frac{A^2e^2}{8\pi m} \left(\frac{\pi}{2} + \tan^{-1} \frac{f}{2\pi\nu_m h} \right),$$

$$= \frac{A^2e^2}{8m},$$

since f is large compared with $2\pi\nu_m h$. We assume that the intensity of the spectrum of the incident light does not vary rapidly with the wave-length.

If $I d\nu$, as before, represents the energy contained within the range of frequency $d\nu$, which passes through one square centimetre per second,

$$I = \frac{cA^2}{8\pi},$$

since $A^2/8\pi$ is the rate of change of the mean value of the energy per unit volume with frequency. Consequently the energy absorbed per electron per second is

$$\frac{\pi e^2 I}{mc},$$

the same result as was obtained by the other method in (8) above. The free period of vibration of the electrons does not enter into the result. The proof is naturally given in a shortened form here; it will be made clearer by consideration of the passages referred to in Planck's 'Wärmestrahlung.'

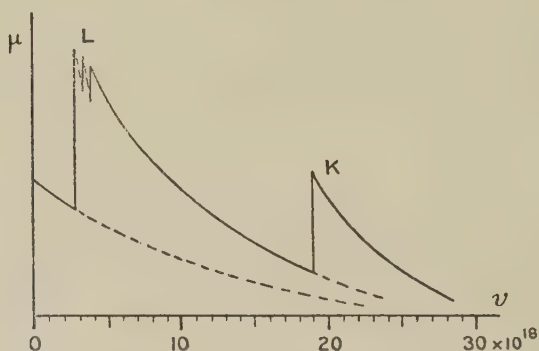
On the one way of deriving the result we assume that the electron starts from rest and that a large number of periods elapse before it loses its energy; as, however, all possible combinations of displacement and velocity may occur, and as the energy increases simply with the time, the initial condition does not affect the result. On the other way, the electron is losing energy uniformly all the time. We cannot prove that the formula holds for the intermediate case—discontinuous losses of energy at short intervals.

Application of the Formula.—The diagram (fig. 1) represents μ as a function of ν for platinum schematically, the K absorption being exaggerated for the sake of a clear diagram.

There are two sharply marked L and K edges from which the absorption gradually falls away in the direction of increasing frequency, and inside the L absorption there are two other edges.

In order to apply formula (4) to calculate p , i. e., the number of electrons per molecule associated with each absorption, it is necessary first to determine $\int \mu d\nu$, i. e., the portion of the area of the curve associated with each absorption. This is not easy. In the first place, the observations at our disposal are not numerous, and it is necessary both to interpolate and extrapolate. Second, it is difficult

Fig. 1.



to know how much of the area to allow to each band. The dotted lines show how I have done this, and there is a certain amount of arbitrariness attaching to the proceeding. Table I. shows the results I have obtained.

I have taken the data for Ag, W, Pb, Bi, and the K absorption of Pt and Au from the paper by S. J. M. Allen*, the data for Al from Siegbahn's "The Spectroscopy of X-Rays," the data for Mo from A. H. Compton's "Secondary Radiations produced by X-Rays" (Bulletin of the National Research Council), and the remaining data from the tables in Kaye's "X-Rays." The columns marked "Area" are the areas $\int \mu/\rho d\nu$, where ρ is the density of the material, since the tables give μ/ρ and not μ , and they are in each case a first attempt. The value for Br is obtained from ethyl bromide. The last two columns give the number of electrons per atom worked out by the formula. The mean result for the thirteen K absorptions is 1.03.

* Phys. Rev. xxiv. p. 1 (1924).

TABLE I.

Element.	Area.		No. of electrons.	
	K.	L.	K.	L.
Al	915×10 ¹⁸		1·52	
Fe	303		1·06	
Ni	275		1·01	
Cu	247		·98	
Zn	252		1·02	
Br	109		·74	
Mo	221		1·32	
Ag	248		1·68	
W	97		1·11	
Pt	75	400×10 ¹⁸	·91	4·8
Au	65	390	·79	4·8
Pb	55		·71	
Bi	39		·51	

This result must be significant. The value of the area varies all the way from 915×10^{18} in the case of Al to 39×10^{18} in the case of Bi, and yet the result comes out approximately constant, showing that we have to deal with a true correlation and not a chance agreement. In the light of the final result the areas might have been apportioned so as to give a much better agreement. There are not enough observations for the L-absorption to state what the 4·8 is an approximation for.

It seems desirable that more measurements should be made of the absorption coefficients, so that the formula may be tested more thoroughly.

Discussion of the Theory.—Theories of the absorption of X-rays have been given from a radically different standpoint*. It is not claimed that the assumption made in this paper of slightly damped electronic oscillators of natural frequencies distributed between the critical absorption frequency and infinity, which are all absorbing energy all the time, constitutes a theory in itself. It is only part of the mechanism. We shall proceed to consider the reasons which lead to this conclusion.

The motion of an electron oscillating about a position of rest may be represented by

$$m \frac{d^2x}{dt^2} + fx = 0.$$

* L. de Broglie, *Jour. de Phys. et Rad.* iii. p. 33 (1922); *C. R.* clxxi. p. 1137 (1920). H. A. Kramers, *Phil. Mag.* xlvi. p. 836 (1923).

Owing to its motion the electron will radiate energy; allowing for the back pressure of the radiation in the equation, we obtain

$$m \frac{d^2x}{dt^2} - \frac{2}{3} \frac{e^2}{c^3} \frac{d^3x}{dt^3} + fx = 0.$$

If the frequency is ν , this may be written

$$m \frac{d^2x}{dt^2} + \frac{2e^2}{3c^3} (2\pi\nu)^2 \frac{dx}{dt} + fx = 0.$$

So the equation has the same form as the left-hand side of (2), if

$$h = \frac{2e^2}{3c^3} (2\pi\nu)^2.$$

Let us assume that $x = l \sin 2\pi\nu t$.

Then the rate at which energy is being radiated is

$$h \left(\frac{dx}{dt} \right)^2 = h l^2 (2\pi\nu)^2 \cos^2 2\pi\nu t,$$

the mean value of which is $2hl^2\pi^2\nu^2$. On substituting for h the energy radiated in one-half period is

$$\frac{8}{3} \frac{\pi^4 \nu^3 e^2 l^2}{c^3}.$$

The maximum value of the kinetic energy is

$$\frac{1}{2} m l^2 (2\pi\nu)^2.$$

So the fraction of the energy radiated in one-half period is

$$\frac{4}{3} \frac{\pi^2 e^2 \nu}{m c^3} = 1.2 \times 10^{-22} \nu.$$

Hence the rate of decay of the energy of the electron may be represented by

$$\exp. (-2.4 \times 10^{-22} \nu^2 t).$$

If the frequency is that of Na light, the energy falls to one-tenth of its value in 3.8×10^{-8} sec. For the case of X-rays of wave-length 1 Å.U., the energy is lost 3.6×10^7 times as fast.

According to (3) the rate at which an electron absorbs energy is

$$\frac{\pi e^2 I}{m c} = 0.0262 I.$$

Suppose that the frequency of the electron is in the

visible spectrum, and that it is exposed to an illumination of 1 metre-candle. The energy received by a surface at a distance of one metre from a Hefner lamp is 2.15×10^{-5} gm. cal. per sq. cm. per sec. About 1 per cent. of this is radiated as light. The difference in frequency between the ends of the visible spectrum is 3.75×10^{14} . Consequently, taking the average value for the visible spectrum,

$$I = \frac{2.15 \times 10^{-7} \times 42 \times 10^6}{3.75 \times 10^{14}} = 2.41 \times 10^{-14},$$

and the energy absorbed per second is

$$0.262 \times 2.41 \times 10^{-14} = 6.35 \times 10^{-16} \text{ erg.}$$

If we take 3.6×10^{-12} as the average value of the quantum for the visible spectrum, the time required to absorb one quantum is about 157 hours. The time required to lose nine-tenths of a quantum is only 3.8×10^{-8} sec. Clearly the balance between emission and absorption takes place at a very small fraction of the quantum. Let us denote this fraction by x . Then its value is obtained from the following equation

$$6.35 \times 10^{-16} = x 3.6 \times 10^{-12} \times 2.4 \times 10^{-22} \nu^2,$$

which gives $x = 2.43 \times 10^{-12}$.

Thus, if the electron were exposed to the light-wave its energy would gradually increase and the radiation loss would simultaneously increase, until the energy reached a value somewhat greater than one-billionth of a quantum. Beyond this there would be no increase. The chances of the electron acquiring a quantum of energy must be much worse in the X-ray spectrum, since both the quantum and the radiation loss are much larger in that region.

But we know that the photo-electrons excited by X-rays have one quantum of energy. The energy must therefore be taken from the absorbing electron and transferred to some other system, while the radiation loss from the former is still a long way below its rate of absorption, and must pass from this other system to the photo-electron.

We thus arrive at the escapement theory of Sir Joseph Larmor*. He regards the electronic radiator as analogous to the pendulum of a clock driven by the energy of a coiled spring which is fed into the motion by an escapement, only his model is reversible; the pendulum may feed its energy

* Phil. Mag. xlii. p. 592 (1921).

back through the escapement into the spring. This analogy applies to our problems well.

The question arises as to the extent of spectrum from which each electron absorbs its energy. Let us go back to equation (2)

$$m \frac{d^2x}{dt^2} + h \frac{dx}{dt} + fx = -eX,$$

assume that we are dealing with one free period, and define the breadth of the band in the absorption spectrum as the difference between the wave-lengths for which the coefficient of absorption has half its maximum value. Then it may be shown (*cf.* my book on 'Light,' p. 433), that this is equal to

$$\frac{h\lambda^2}{2m\pi c}.$$

If we assume that the loss of energy is wholly a radiation loss and substitute the appropriate value of h , this becomes

$$\frac{4\pi}{3} \frac{e^2}{mc^2},$$

the numerical value of which is 1.16×10^{-4} Å.U. This is a breadth much too small to observe.

Now we know that the radiation loss is only part of the loss. The " h " must cover in addition the removal of energy by the "escapement." Hence its value must be greater than the figure we have assumed, but not very much greater, and consequently the bands, broader than the breadth we have arrived at, but not much broader.

To conclude: the picture at which we arrive at is this. If we take, for example, the case of Fe, within the region of the K absorption, 25 of its 26 electrons are taking energy from the incident rays and "scattering" it, losing it by resonance radiation. The remaining electron absorbs energy from a narrow region somewhere between the head of the band and infinite frequency; it scatters a small proportion of this energy but transmits most to another system of which we know nothing. Its own energy never becomes more than an insignificant fraction of the appropriate quantum. Outside this limited region the remaining electron "scatters" as well as the others.

April 2, 1926.

XLIV. *The Magnetic Stability of Permanent Magnets.*

By ROBERT COCHRAN GRAY, M.A., D.Sc.*

Introductory.

A PIECE of steel, after magnetization, experiences a gradual loss of magnetism, the rate of loss tending to zero only after the lapse of several months. The process of *ageing*, either by heat treatment, vibration, or partial demagnetization, or by all of these, represents an attempt to bring the magnet into its final stable state in a few hours instead of months. This paper gives the effect of each of these treatments on the magnetic stability of a magnet.

Mechanical Stability and Magnetic Stability.

It is important to distinguish carefully between *mechanical stability* and *magnetic stability*. Strains in the material gradually disappear, and partial recrystallization takes place, altering the nature of the material; and during these changes, and because of them, the magnetic quality alters. This mechanical stabilization should be complete before the material is magnetized. In magnetic stabilization the principle is that of subjecting the magnet, before use, to a treatment equivalent to that which it will experience when in use. How the nature of this experience may be evaluated will be indicated later. This paper refers to materials already mechanically stable; such materials were available for test in the form of cylindrical magnets that had been in use in a first-year students' laboratory for from ten to forty years.

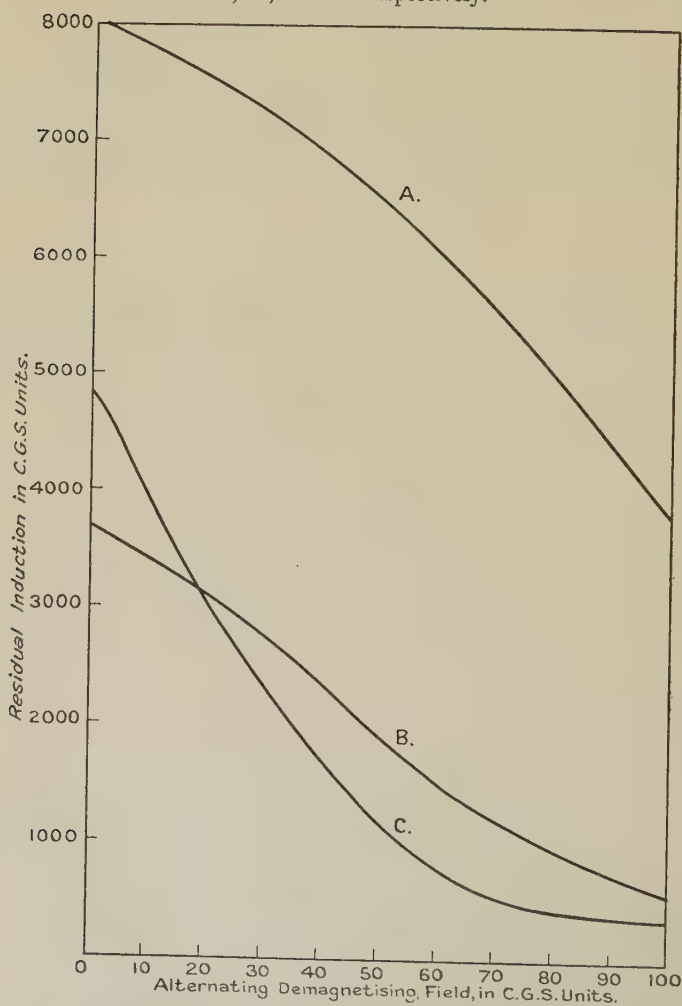
Effect of Demagnetization.

The only safe method of demagnetization is to subject the magnet to an alternating field, beginning at a definite value to be here called the *demagnetizing field*, and to reduce this gradually to zero. If we magnetize a specimen to saturation, and then apply a small demagnetizing field in this way, we remove a small amount of the magnetism; each successive increase in the demagnetizing field (see fig. 1) causes an additional loss. The greatest loss of magnetism for a given small increase in the demagnetizing field occurs when the demagnetizing field is slightly less than the saturation coercive force (H_{cs}) of the material. The figure gives the

* Communicated by the Author.

curves obtained from three materials A, B, C, of coercive force 113, 60, 34 respectively. Material A was permanite. The application of a demagnetizing field equal to the coercive

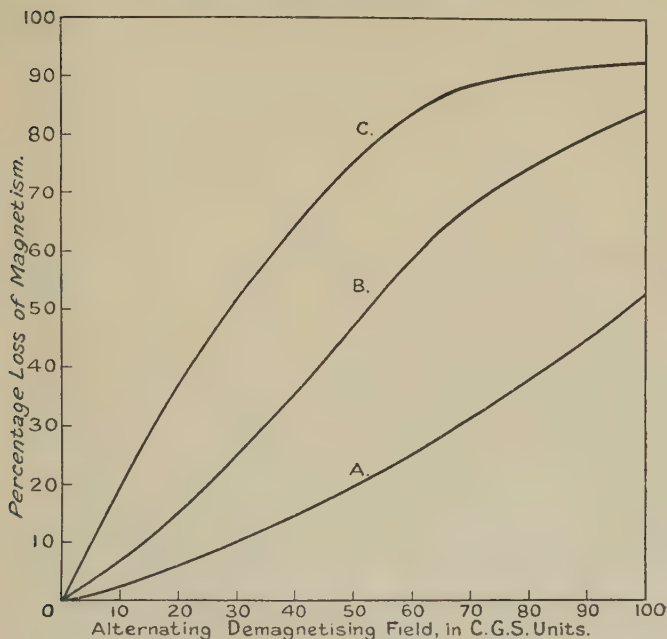
Fig. 1.—Showing decrease in magnetism for various alternating demagnetizing fields. Materials A, B, C had coercive force 113, 60, 34 units respectively.



force of the material results in a reduction of the residual induction by over 50 per cent., and near this field the curve is steepest. Thus, it is most important that material for permanent magnets should have, in addition to a high residual

induction, as high a coercive force as possible. The percentage loss of magnetism for different demagnetizing fields is given in fig. 2, where the effect of high coercive force in keeping down the loss is more apparent. For example, a demagnetizing field of 50 units reduces the residual induction by 19, 48, 75 per cent., for the materials of coercive force 113, 60, 34 units respectively. Further,

Fig. 2.—Showing percentage loss of magnetism for various alternating demagnetizing fields.

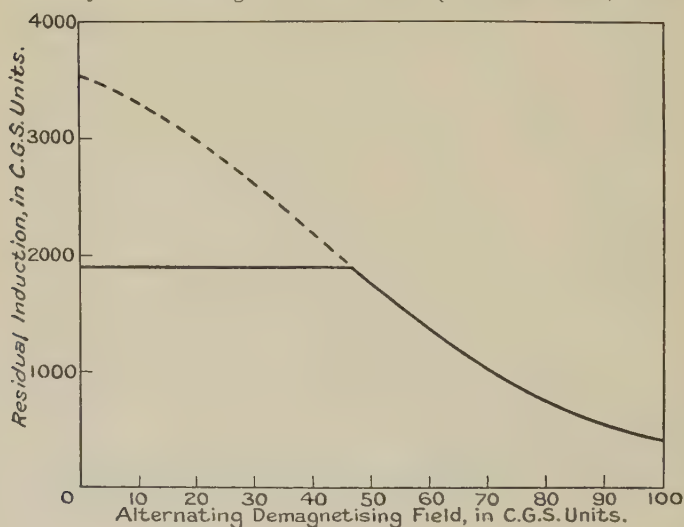


it is quite possible that a material of high coercive force and comparatively low residual induction may possess, when stabilized by the proper demagnetizing field, a larger amount of magnetism than a material of much higher residual induction but of lower coercive force. Reference to fig. 1 will show that material B, of initial residual induction only 75 per cent. of that of material C, retains after the application of fields greater than 20 units more magnetism than material C; this effect is due to the higher coercive force possessed by material B. Such material of higher coercive force will be less affected in practice in the

event of its experiencing larger demagnetizing fields than had been expected ; this is indicated by the smaller gradient, for moderate fields, of the curve of B compared with the gradient of the curve of C.

If a demagnetizing field of, say, 50 units has been applied to a magnet, no subsequent demagnetizing field of amount less than 50 units will have any effect on the magnetism. On this fact is based the method of magnetic stabilization by partial demagnetization. The *stabilizing field*, i. e. the initial value of the demagnetizing field, should be that likely to be experienced by the magnet when in use. The demagnetization curve is then of the type shown in fig. 3, where the

Fig. 3.—Showing the magnetic stability due to partial demagnetization by an alternating field of 47 units. (Continuous line.)



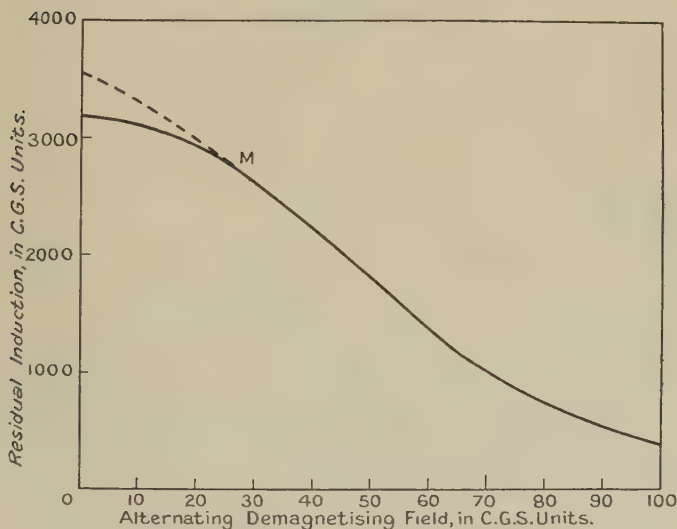
stabilizing field is 47 units. The first portion of the curve is horizontal, representing magnetic stability ; the remainder of the curve beyond the stabilizing field follows the original curve.

Effect of Steaming.

Stabilization against variations of temperature consists of keeping the specimen at 100° C. for an hour, then at room temperature for an hour, and continuing this alternation until the magnetism attains a steady state, usually after three or four such cycles. The changes in volume, and slight

softening, alter the fields controlling the elemental magnets, with the result that part of the residual induction disappears. When there is taken a demagnetization curve of a specimen stabilized in this way, we find that small demagnetizing fields have a small but appreciable effect (see fig. 4); this effect remains small until a definite field M is reached, after which the effects are large and the curve follows the usual run. For the specimen whose curve is given in fig. 4, this

Fig. 4.—Showing the effect of steaming a magnet.
(Continuous line.)



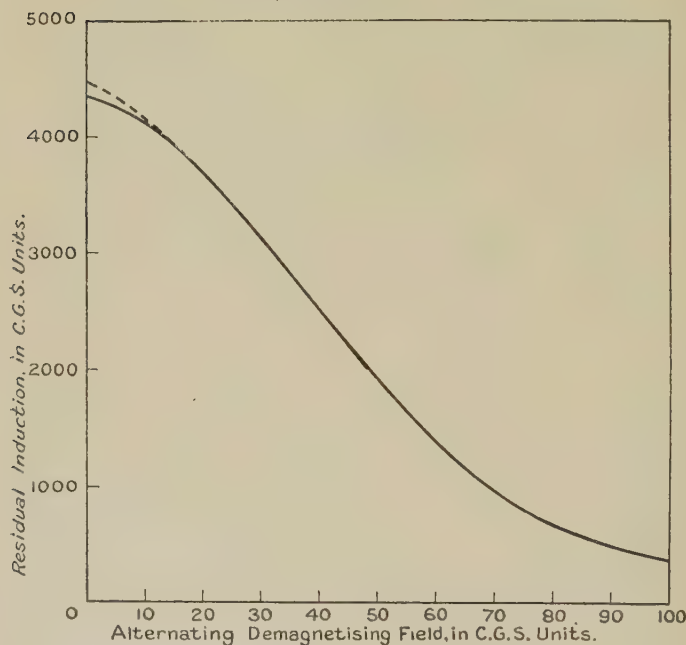
field M was about 29 units. The important point here is that if the material, before steaming, is demagnetized by a field greater than M , steaming has no effect: the partial demagnetization has stabilized the material against variations of temperature.

Effect of Vibration.

The effect of vibration on the magnetism of a specimen is very similar to that of steaming. A rod was magnetized, then dropped fifty times, on alternate ends, a height of one foot, on to a stone floor, and caught on the rebound. The demagnetization curve is shown in fig. 5; it will be seen that the curve joins the original curve at a field of about 12 units. When the material was initially demagnetized by

a field greater than this, vibration had no effect. Thus stabilization against vibration, like stabilization against

Fig. 5.—Showing the effect of vibrating a magnet.
(Continuous liné.)



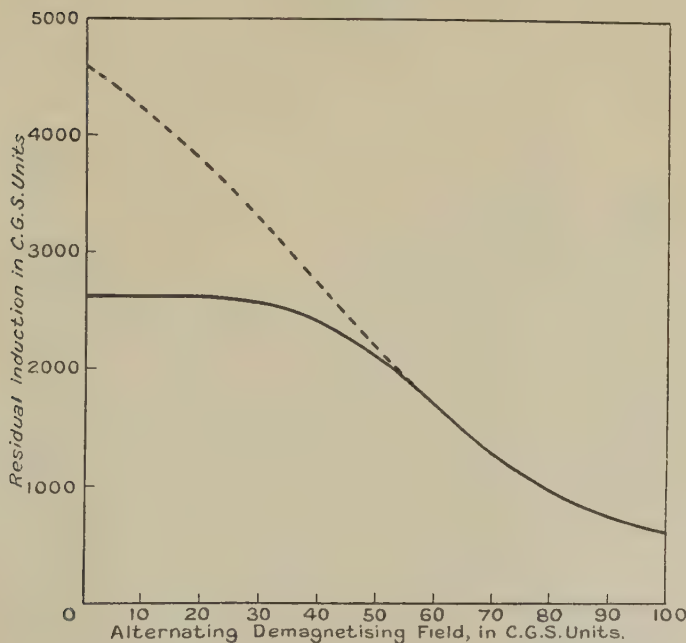
small variations in temperature, may be carried out most easily by demagnetization by a suitable field.

Effect of Time.

All the specimens, except the permanite, used in these tests had been magnetized some years ago, and each had lost a proportion of its original magnetism. The demagnetization curve of a typical specimen in this "naturally aged" state is shown in fig. 6. It will be seen that for this specimen the curve meets the main curve, which was taken after subsequent re-magnetization, at a field of about 53 units. This field lay, in every case, between 52 and 57 units, the average being 55, which is the equivalent therefore of the demagnetizing treatment experienced in practice by an ordinary binnacle magnet treated with little care. But while this "field of experience" was nearly constant, the

percentage loss of magnetism varied within the wide limits of 35 and 60 per cent. It is interesting to note that the permanite specimen, magnetized by the makers, and stabilized partly by them, presumably, and partly by two years' use, showed a field of experience of 54 units and a percentage loss of 20 per cent. Comparison of the loss and the coercive force in all these cases showed that the law that "the percentage loss is inversely proportional to the coercive force"

Fig. 6.—Showing the effect of time on a magnet.
(Continuous line.)

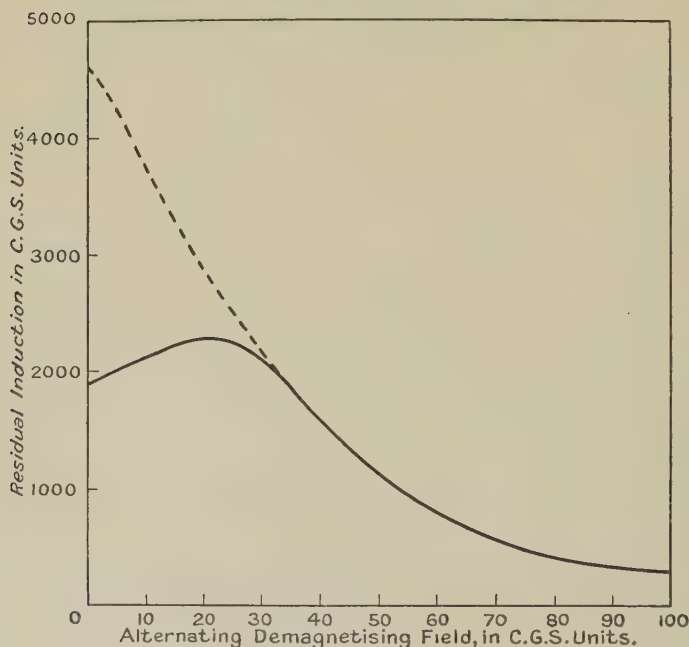


is approximately true within the conditions covered by these tests; if this law held for a coercive force of 225 units, we should expect a loss of magnetism of only 10 per cent. after the lapse of years. The rule in magnetic stabilization should therefore be partial demagnetization by a definite field, rather than the removal of a definite percentage of the residual induction. It is extremely probable that our specimens, if magnetized to saturation and then demagnetized by a field of 55 units, would show no appreciable loss of magnetism with time

Effect of Partial Magnetization in the Opposite Sense.

It might be expected that the reduction in magnetism that is necessary for stabilization might most easily be effected by applying a field, of properly chosen amount, in the opposite direction to the original magnetizing field. This method cannot be recommended. Fig. 7 gives the demagnetization

Fig. 7.—Showing the effect of applying a weak field to a magnet, in the direction opposite to the original magnetization.



curve of a specimen that had been magnetized in one direction by a field of 280 units and had then been exposed to a field of 34 units in the opposite direction. It will be noticed, apart from the peculiarity that for low fields the process of "demagnetization" actually increases the magnetism of the specimen, that the magnetism is affected even by small demagnetizing fields. A comparison of figs. 3 and 7 will show the decided advantage in stability attained by partial demagnetization by means of an alternating decreasing field.

Conclusion.

It has been mentioned that these rod magnets had experienced, when in use, demagnetizing fields averaging 55 units.

One of these magnets partially demagnetized by a field of 29 units was unaffected by steaming; another, partially demagnetized by a field of 12 units, was unaffected by moderate vibration. Hence for complete magnetic stability of these magnets it is necessary and sufficient that a demagnetizing field of 55 units should be applied. Steaming and vibration are probably necessary in order to stabilize the material mechanically, and thus will affect indirectly the magnetic constants (*e. g.* coercive force); but they have no direct use in magnetic stabilization after mechanical stabilization, since their effect is more than covered by the partial demagnetization necessary to render the material immune to the effects of the demagnetizing fields likely to be experienced by the magnet when in use.

Summary.

A distinction is made between the stabilization of the *material* intended for permanent magnets, and the stabilization of its *magnetism*. After the material has been mechanically stabilized, it should be magnetized to saturation and then demagnetized by an alternating decreasing field whose maximum value is slightly above that of the field likely to be experienced when the magnet is in use. A method of finding the value of this latter field is given. This partial demagnetization stabilizes the magnet not only against demagnetizing fields, but also against temperature variations and against moderate vibration. The importance of a high coercive force is indicated; the percentage loss of magnetism with time is, approximately, inversely proportional to the coercive force.

XLV. *Absorption and Resonance Radiation in Excited Helium and the Structure of the 3889 Line.* By W. H. McCURDY, *Ph.D., National Research Council Fellow in Physics* *.

Plate IX]

INTRODUCTION.

PASCHEN† observed that a column of weakly excited helium showed marked absorbing power for light of wave-length equal to that of the first term of the principal

* Communicated by the Author.

† Paschen, *Ann. d. Phys.* xlv. p. 625 (1914).

series of both systems of the helium spectrum, $10830\text{ \AA}$ and $20852\text{ \AA}$ respectively. Further, that resonance radiation of wave-length $10830\text{ \AA}$ was produced in the weakly excited gas by the monochromatic radiation of that wave-length from a second helium discharge tube. Absorption of light of wave-length corresponding to transitions from other than the normal state of the atoms involved has been frequently observed. Ladenburg* and others have observed marked absorption of the Balmer series in a strong discharge in hydrogen. Compton and Turner† have observed absorption of several lines of which the initial state in absorption is $2p$ and the final a higher s state.

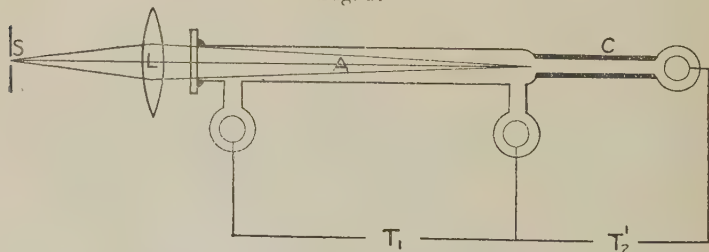
More recently Meissner‡ has made a more detailed study of the absorption in weakly excited neon. He has observed absorption of twenty-six lines having initial states in absorption $2s_i$, where i varies from 2 to 5 inclusive. He has not observed any absorption for lines of which the initial state is a p level.

The following is a report of an investigation of a more general nature of the optical properties of excited helium. The absorption of most of the helium lines between $6678\text{ \AA}$ and $3614\text{ \AA}$ has been investigated, and photographs showing the existence of resonance radiation of wave-length $3889\text{ \AA}$ have been obtained.

METHOD.

The arrangement of apparatus used in the work is shown diagrammatically in fig. 1. The capillary C served as

Fig. 1.



source of light, and the larger part of the tube A served as the absorbing column, which was about 80 cm. in length.

* Ladenburg, *Verh. d. Deutsch. Phys. Ges.* x. p. 580 (1908), & xii. p. 54 (1910); also Kimura and Nakamura, *Jap. Journ. of Phys.* ii. p. 53 (1923), and Hulbert, *Phys. Rev.* xxvi. p. 124 (1925).

† Compton and Turner, *Phys. Rev.* xxv. p. 606 (1925).

‡ Meissner, *Ann. d. Phys.* lxxvi. p. 124 (1925).

The two portions of the tube could be excited independently by means of the two transformers T_1 , T_2' giving 6000 to 10,000 volts on the secondary, with 120 volts 60 cycle A.C. on the primary. The current in either tube could be varied at will by means of a resistance in series with the primary of the transformer without appreciably influencing the other. The electrodes were of aluminium foil and were freed from hydrogen by running a discharge for some time before introducing the helium. The helium used was stored over water and dried by phosphorus pentoxide and purified by standing for some time in charcoal immersed in liquid air. No trace of hydrogen could be observed visually in examination of the tube spectrum.

The end of the capillary C was focused on the slit of the spectrograph S by means of the lens L placed as near the end of the tube as possible, thus eliminating the radiation from the absorbing column as much as possible. It is, of course, impossible to eliminate this completely, but the above arrangement appeared satisfactory. The observing system consisted of a glass echelon grating of twenty steps each of thickness about 6 mm. A glass prism of about 7 cm. base was used to separate the lines. In making the photographs, a four-foot photographic objective was used and Hammer rapid plates for the spectral region in which they are sensitive.

The object of using this method was to avoid the necessity of making photometric determinations of the density of the plates obtained, since the absorption appeared as the reversal of the line observed. As an indication of the degree of absorption the width of the reversal was observed. This method would of course not be satisfactory for detailed or accurate investigation, since the maximum width of the reversed portion of the line is equal to the width of the emission line in the absorbing column, which is probably less than that of the line from the capillary due to the lower temperature of the absorbing column and also to the lower field strengths in the larger absorbing tube. This, however, is probably sufficient for the approximate results desired, especially since no extreme care was taken to eliminate all impurities from the helium, which obviously detracts from the theoretical values of the results. All that can be said is that there was not sufficient impurity present to show spectroscopically, in visual observations.

A series of exposures of equal times were made on one plate with gradually increasing current in the absorbing column, starting from zero. By this method the effect of the current

in the absorbing column was quickly and easily determined. The process was repeated for most of the lines between $6678 \text{ \AA}$ and $3614 \text{ \AA}$ and for pressures of helium between 9.8 mm. and 0.8 mm. Owing to the fact that it was impossible to eliminate completely the glow in the absorbing column with this arrangement of apparatus, it was never possible to obtain a photograph of the unreversed 3889 line.

RESULTS.

It was found that not only the $1S-mP$ and $1\sigma-m\pi$ series, but also the $1P-mD$ and $1\pi-m\delta$ showed strong absorption. It was found impossible, however, to detect any trace of absorption in the case of the $1P-mS$ or $1\pi-m\sigma$ series. Table I. has been prepared showing the results that were obtained at a pressure of 4 mm. The amount of the absorption is estimated from the width of the reversal of the line as already indicated.

TABLE I.

Absorption of the helium lines in a column of helium² of length about 80 cm. excited by A. C. Current density of the exciting current about 100 m. amps. per cm^2 . Pressure of the helium 4 mm.

Wave-length.	Line.	Absorption.
$6678 \text{ \AA}$.	$1P-2D$	Weak (only under extreme conditions).
4922	$1P-3D$	Very weak (only under extreme conditions).
4387	$1P-4D$	Not detectable.
5016	$1S-2P$	Strong.
3964	$1S-3P$	Weak.
3614	$1S-4P$	Very weak.
3889	$1\sigma-2\pi$	Very strong.
3187	$1\sigma-3\pi$	Strong.
5276	$1\pi-2\delta$	Strong.
4471	$1\pi-3\delta$	Fair.
4026	$1\pi-4\delta$	Weak.
3819	$1\pi-5\delta$	Very weak.

No absorption was to be found for any other lines in the region considered between $6678 \text{ \AA}$ and $3187 \text{ \AA}$.

It will be observed that the principal series of both systems shows a greater absorption for corresponding terms

than does the subordinate series. This is to be expected, since the principal series are stronger in emission than are the subordinate series. It is also to be expected that the $1P-mS$ and $1\pi-m\sigma$ series should show little absorption since they are comparatively weak in emission. The result shows very clearly, however, that there are two factors involved in the consideration of the emission and absorption spectra of gases. Since both subordinate series have the same initial state, the number of the atoms in a state to absorb the two series is the same. Still the one series shows strong absorption while the other shows none. Thus the factor involving the probability of a given transition must play fully as important a rôle as the concentration of atoms in a state initial to the transition considered. This is still further emphasized by the results on different lines of a given series.

Effect of Excitation on the observed Absorption.—Figs. 1, 2, 3, 4, 5, and 6 (Pl. IX.) show the absorption of different lines under different pressure conditions. Diagrams *a* to *d* are taken with increasing current in the absorbing column. It is apparent that the width of the reversal of the line increases with the current in the absorbing column. At high current densities in the absorbing column, however, the width of the reversal appears to decrease. This is probably due to the contribution of the absorbing column to the observed radiation. If this could be entirely eliminated, it is probable that the width of the reversal would increase with the excitation of the absorption tube until the state was reached where the reversal was equal in width to the emission line of the absorbing column. The results show, however, a marked increase in the absorption with an increase in the excitation of the absorbing column.

Absorption of Series.—In the case of the $1S-mP$ series Paschen* observed absorption of the first term of the series. The present investigation has shown observable absorption to the fourth term 3614 Å . The width of the reversal is found to fall off rapidly as the higher terms of the series are studied. In reproducing the results in enlargements only the second and third terms have been used. Comparing this with the observed reversal of the $1P-mD$ series, it was found that reversal could be observed only to the second term, and only with intense excitation in the absorbing column. Observations on these were made visually since the first term is in the red, 6678, which require the use of red sensitive

* Paschen, *loc. cit.*

plates. Thus it appears that the rate at which the absorption falls off is less for the principal than for the subordinate series. The same would probably be true in the case of the doublet system also if observations were sufficiently extensive. In fig. 5 (Pl. IX.) is shown the reversal of the $3964 \text{ \AA}$ line under conditions comparable with those under which the results on the $5016 \text{ \AA}$ line shown in fig. 3 were obtained. Fig. 6 shows the reversal of the yellow line $5876 \text{ \AA}$, but it is not comparable with the photographs of the $3889 \text{ \AA}$ line shown in figs. 2 and 4 (Pl. IX.). In the case of the doublet system observations showed absorption to the fourth term of the subordinate series while, up to the present at least, observations have been made only on terms up to the third of the principal series, so no conclusions can be drawn from the comparison of the results on the two series.

Effect of Pressure.—Figs. 1 and 2 (Pl. IX.) show the reversal of the corresponding lines of the two systems $5016 \text{ \AA}$ and $3889 \text{ \AA}$ respectively at 9.8 mm. pressure , and figs. 3 and 4 the same at $.8 \text{ mm. pressure}$. Though the enlargements do not show the results as distinctly as the original plates, still it may be observed that the reversal in the case of the line $3889 \text{ \AA}$ is wider at the higher pressure while the reverse is true of the line $5016 \text{ \AA}$. Thus it appears that the pressure has a great effect on the absorption of the different series. It is as should be expected from the emission spectra of the gas under different pressures. At high pressures the doublet system is predominant, giving the discharge a distinctly yellow colour, while at low pressures the singlet system predominates and the discharge has a greenish tinge. Thus it is to be expected that the singlets will be absorbed more strongly at low pressures and the doublets more strongly at high pressures.

As was stated in the preceding paragraph it was possible to reproduce the reversal of the $3964 \text{ \AA}$ line only at low pressures. A similar result was obtained in the case of the doublet system, in which it was found that the absorption appeared to fall off more rapidly at low pressures than at higher ones. Detailed investigation of this sort, however, would be justified only with the use of very pure helium and under conditions more reproducible than is possible using transformer excitation and ordinary purification processes.

Effects of Impurities.—The effect of hydrogen on the absorption is clearly shown by comparison of figs. 4 and 7 (Pl. IX.)

Fig. 7 (Pl. IX.) shows the reversal of the 3889 Å line when the spectrum of the discharge showed the Balmer lines of hydrogen distinctly, while fig. 4 shows the reversal of the same line under similar pressure in helium, pure enough to render the Balmer lines invisible. It is apparent that hydrogen greatly reduces the absorption. This is in agreement with the results obtained by Paschen * and Meissner†.

The effect of the impurity is probably a reduction of the life of an excited atom. The assumption that this was the case was made recently in considering the cause of striations in the positive column of a discharge ‡, and this appears to be a partial confirmation of that hypothesis. In this case the excited atom of helium contains sufficient energy to ionize the hydrogen in collisions of the second kind.

STRUCTURE OF THE 3889 LINE.

Examination of the photographs of the reversed 3889 line showed that the reversal was not symmetrical, indicating an unresolved component on the short wave-length side of the line. It was thus decided to look for another component to the line. For this work a quartz Lummer-Gehrcke plate was used and the tube which served as the source of light was cooled by wrapping it with cotton which was kept wet with liquid air. This, together with a very low current in the tube, produced a line much narrower than was observed in the absorption experiments.

An enlarged photograph of the fringes produced by the line is shown in fig. 9 (Pl. IX.). This shows, as was expected, that there is a weak component on the short wave-length side of the line. The separation of this component from the main component of the line as calculated from the dimensions of the plate was found to be $\cdot 044$ Å. This was checked by use of a second plate of different dimensions. Thus assuming the wave-length of the line as given in the tables to be that of the strong component, the wave-length of the weak component comes out to be 3888·602 Å.

RESONANCE RADIATION IN THE WEAKLY EXCITED HELIUM.

The extremely strong absorption in the excited helium of the 3889 Å line indicated the possibility of detecting resonance radiation of this wave-length, if the weakly

* Paschen, *loc. cit.*

† Meissner, *loc. cit.*

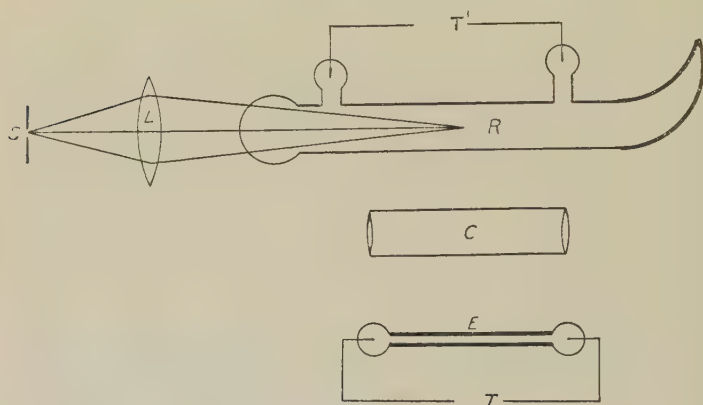
‡ McCurdy, *Phil. Mag.* xlviii. p. 898 (1924).

excited gas was subjected to strong monochromatic radiation of this light. Paschen observed resonance of the first line of this series by means of a thermopile and it was considered worth while to attempt to photograph resonance of the second line.

Method.

The method used needs little description. The apparatus is shown diagrammatically in fig. 2. The capillary tube E filled with helium to about 4 mm. pressure served as a source of monochromatic radiation, while the tube R, filled to 3.6 mm. pressure, served as resonance tube. The two tubes were excited by means of transformers as in the previous work on absorption.

Fig. 2.



The light from the capillary E was focussed along the axis of the resonance tube R by means of the cylindrical lens C. The radiation from the resonance tube was focussed on the wide slit of a small quartz spectrograph S by means of the lens L, placed at a considerable distance from the tube in order that as much of the length of the tube as possible should contribute to the observed radiation. In order to eliminate, as far as possible, light reflected from the sides of the tube, the end was drawn off as shown and painted black. Since the light from the emission tube was focussed along the axis of the resonance tube, any resonance radiation should be observed as an increase in the intensity of the light from the central portion of the tube.

In making the observations, three exposures of equal time were made on a single plate. Thus no errors were introduced in the process of developing. The first exposure was made with a weak discharge flowing in the resonance tube and the light from the capillary screened off by placing a black screen between the two tubes. This exposure gave the intensity of the radiation due to the electrical excitation of the resonance tube. The second exposure was taken with the same current flowing in the resonance tube but with the screen removed. Thus the radiation observed in this case consisted of that due to electrical excitation and also that due to the resonance produced by the light from the emission tube E. A third exposure was made with no current flowing in the resonance tube but with the emission tube running and the screen removed. This would prove whether or not there was an appreciable amount of scattered light from the emission tube reaching the spectrograph.

Results.

Fig. 8 (Pl. IX.) shows the results of the experiments. It was found that no trace of scattered light was to be observed on the plates. The exposures were of only 90 seconds and the scattered light was not of sufficient intensity to be observed. The results show, however, a distinct increase in the intensity of the light when the radiation from the tube E is incident on the resonance tube. This must be due to resonance produced by the light of the same wave-length, $3889 \text{ \AA}$, from the emission tube. In fig. 8, *a* is the 3889 line of the resonance tube alone and *b* is with the screen removed. The central portion of the line in fig. 8*b* is seen to be increased in intensity in comparison with fig. 8*a*.

Visual observations were made on the green line, $5016 \text{ \AA}$, but it was found that no apparent increase occurred under the action of the light from the tube E. It is possible that observation of resonance radiation of this wave-length may be successful under more favourable conditions. These should consist of very low pressure and extremely pure helium, in order that the absorption for this light may be very strong. It is very probable that resonance radiation of wave-length $3187 \text{ \AA}$ would have been detected had the apparatus used been of quartz, but it was not considered advisable to construct tubes of quartz for the work.

SUMMARY.

Results of these experiments on the optical properties of excited helium may be summarized as follows:—

(1) Excited helium shows marked absorption for terms of both the principal and diffuse subordinate series of the two systems of the helium spectrum.

(2) Resonance radiation of wave-length 3889 Å has been observed in the weakly excited gas under the influence of monochromatic radiation of this wave-length.

(3) Examination of the structure of the 3889 line of helium has shown it to be a doublet in agreement with the rest of the spectral system. The second component is weak and of wave-length 0.044 Å less than the main component.

In conclusion the author wishes to express his thanks to Prof. R. W. Wood for his suggestions throughout the work, and also to the National Research Council for the award of a Fellowship which made the investigation possible.

Johns Hopkins University,
Baltimore, Md.,
February 20th, 1926.

XLVI. *On the Determination of the Velocity Constant of a Unimolecular Reaction.* By E. A. GUGGENHEIM, *Wollaston Student, Gonville and Caius College, Cambridge*.*

THE rate of a chemical reaction is frequently determined by observation of some physical property of the system, whose value is a linear function of the concentration of a reacting substance. In the case of a unimolecular reaction, whether reversible or irreversible, if v is the "reading" at time t and if v_0 and v_∞ are the initial ($t=0$) and final ($t=\infty$) readings, then the relation between v and t is

$$v_\infty - v = (v_\infty - v_0)e^{-kt} \quad . \quad . \quad . \quad (1.1)$$

$$\text{or} \quad \log_e \frac{v_\infty - v}{v_\infty - v_0} + kt = 0, \quad . \quad . \quad . \quad (1.2)$$

where k is the velocity constant (in the case of a reversible reaction k is the sum of the constants of the two opposed processes). For the sake of definiteness we shall assume that v increases with t ; if this is not the case it is only necessary to replace v by $-v$, v_0 by $-v_0$, and v_∞ by $-v_\infty$. We shall thus treat $v_\infty - v$ as essentially positive.

* Communicated by Prof. R. H. Fowler, F.R.S., Cambridge.

To determine the value of k it is usual to plot $\log(v_{\infty} - v)$ against t and measure the slope of the straight line so obtained. Other commonly used methods of treatment, such as calculating k from v_{∞} and various pairs of values of v and then averaging the values of k so obtained, are substantially equivalent to the above. They are all alike in giving to v_{∞} a weight at least approximately equal to the sum of the weights given to all the other readings, and an error of $+\epsilon$ in v_{∞} affects the value obtained for k in the same way as a systematic error of $-\epsilon$ (in the same direction) in all the other readings. This treatment is justifiable only if v_{∞} is known with appreciably greater accuracy than the other v 's. This may be so if the final value is observed over a long period after the reaction has practically reached completion. If this is ever carried out in practice, it is the exception rather than the rule.

Not infrequently it is inconvenient or even impossible to observe the end-point directly at all; in such cases it is usual to obtain a value for it by extrapolation. If this is done by any straightforward method the value of v_{∞} so obtained will at the best be no more accurate than any of the directly observed values of v . The best value for k will then not be obtained by any of the usual methods which give great weight to v_{∞} .

Equation (1.1) or (1.2) regarded as that of a v - t curve contains three parameters, k , v_0 , and v_{∞} ; hence three points (v_1, t_1) , (v_2, t_2) , (v_3, t_3) are theoretically sufficient to fix the curve and so determine the values of all three parameters. In a recent paper in this journal* Mr. R. Christie Smith has shown that if the three points be so chosen that the time-interval $(t_2 - t_1)$ between the former pair is equal to that $(t_3 - t_2)$ between the latter pair, then it is easy to eliminate k and v_0 and so obtain v_{∞} as an explicit function of v_1, v_2, v_3 . The equation obtained becomes in our notation

$$v_{\infty} = v_1 + \frac{(v_2 - v_1)^2}{2v_2 - v_1 - v_3} \quad \dots \quad (2)$$

If the values of v_1, v_2, v_3 were known exactly this would be a neat way of evaluating v_{∞} . Actually, owing to the inevitable inaccuracies of the individual readings, it would be essential to apply the process to a large number of such sets of three points and then average somehow: it is not easy to see how this is to be done giving equal weights to all the observed readings. Failing this, the value obtained could not satisfy the criterion of being more accurate than

* Phil. Mag. vol. i. (Feb. 1926).

any of the other readings, and so would not be suitable for the ordinary method of plotting.

In any case it would seem a more natural procedure, instead of eliminating k and v , to eliminate v_0 and v , so obtaining directly for k the very simple formula

$$k = \frac{1}{\Delta t} \log_e \frac{v_2 - v_1}{v_3 - v_2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta t = t_2 - t_1 = t_3 - t_2$.

The following treatment is in principle somewhat similar to this, but is more convenient in practice.

Suppose $v_1, \dots v_i, \dots v_n$ are n readings taken at times $t_1, \dots t_i, \dots t_n$ (without any restriction as to the intervals), and that n more readings, $v_1', \dots v_i', \dots v_n'$, be taken at times $t_1 + \tau, \dots t_i + \tau, \dots t_n + \tau$ each a constant time τ after one of the previous set. Then we have the equations

$$v_\infty - v_i = (v_\infty - v_0)e^{-kt_i}, \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

$$v_\infty - v_i' = (v_\infty - v_0)e^{-kt_i - k\tau}. \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

By subtraction

$$v_i' - v_i = (v_\infty - v_0)(1 - e^{-k\tau})e^{-kt_i}, \quad . \quad . \quad (4.3)$$

or taking logarithms,

$$\begin{aligned} kt_i + \log_e (v_i' - v_i) &= \log_e \{(v_\infty - v_0)(1 - e^{-k\tau})\} \\ &= \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (4.4) \end{aligned}$$

Hence we have only to plot $\log_{10}(v_i' - v)$ against t ; the straight line so obtained will have a gradient $-k \log_{10} e$.

It is to be especially noted that in this treatment every actually observed reading is used once and once only and there is no extrapolation. The longer the constant interval τ the greater the value of $v' - v$ for a given t and the more accurate the method. Provided τ is several times as great as the time of half completion of the reaction, the accuracy will be of the same order as in taking n ordinary readings and further taking n readings of the end-point spread over an interval of time equal to that spent on the ordinary readings; in fact it is equivalent to obtaining a very accurate end-point and using it in the usual manner.

This method has been used for some time in this laboratory. Its value may be gauged from the two tables which give the results from an actual experiment. The individual readings are correct to $\cdot 01$. The observed end-point was $6.49 \pm \cdot 01$; the value obtained by simple extrapolation is the same, and it is doubtful if any more elaborate method could fix it more exactly without first determining k . In Table I. the

TABLE I.

Time t , H. M. S.	v , ...	$v_{\infty} = 6.48$.			$v_{\infty} = 6.50$.		
		$v_{\infty} - v$, ...	$\log_{10}$ $(v_{\infty} - v)$,	$v_{\infty} - v$ calc.	$v_{\infty} - v$, ...	$\log_{10}$ $(v_{\infty} - v)$,	$v_{\infty} - v$ calc.
10 46 30	3.80	2.68	0.428	2.685	2.70	0.431	2.705
49 0	3.90	2.58	.412	2.68	2.60	.415	2.595
51 45	4.00	2.48	.394	2.48	2.50	.398	2.495
54 15	4.10	2.38	.377	2.39	2.40	.380	2.40
57 15	4.20	2.28	.358	2.28	2.30	.362	2.30
11 0 0	4.30	2.18	.339	2.18	2.20	.342	2.20
3 15	4.40	2.08	.318	2.08	2.10	.322	2.10
6 45	4.50	1.98	.297	1.97	2.00	.301	1.99
10 0	4.60	1.88	.274	1.88	1.90	.279	1.90
13 30	4.70	1.78	.250	1.78	1.80	.255	1.80
17 0	4.80	1.68	.225	1.69	1.70	.230	1.71
21 30	4.90	1.58	.199	1.575	1.60	.204	1.60
25 45	5.00	1.48	.170	1.475	1.50	.176	1.50
30 30	5.10	1.38	.140	1.37	1.40	.146	1.395
35 0	5.20	1.28	.107	1.28	1.30	.114	1.30
40 0	5.30	1.18	.072	1.185	1.20	.079	1.21
46 0	5.40	1.08	.033	1.08	1.10	.041	1.11
52 15	5.50	0.98	.091	0.985	1.00	.000	1.01
12 0 0	5.60	0.88	.944	0.875	0.90	.954	0.90
7 45	5.70	0.78	.892	0.775	0.80	.903	0.80
16 30	5.80	0.68	.833	0.68	0.70	.845	0.70
26 45	5.90	0.58	.763	0.58	0.60	.778	0.60
39 0	6.00	0.48	.681	0.48	0.50	.699	0.50
55 0	6.10	0.38	.580	0.38	0.40	.602	0.41
13 14 0	6.20	0.28					
40 0	6.30	0.18					
14 31 30	6.40	0.08					
18 0 0	6.48						
Next day.....	6.495						
By extrapolation	6.48						

$\log_{10} e \times 10^3 \times k = 6.50 \text{ min.}^{-1}$

$\log_{10} e \times 10^3 \times k = 6.64 \text{ min.}^{-1}$

TABLE II.

Time t , H. M. S.		v .	$\tau = 1\frac{1}{2}$ hrs. v' .			$\tau = 2$ hrs. v'' .			$\log_{10} \frac{v''-v}{(v''-v)}$.		$v''-v$ calc.	$v''-v$ calc.
10	46	30		3.80	2.00	0.301	0.301	0.352	0.352	2.555	2.555	2.555
49	0		3.90	1.92	1.92	.283	1.92	1.92	.337	2.17	2.17	2.17
51	45		4.00	1.855	1.855	.268	1.85	1.85	.320	2.085	2.085	2.085
54	15		4.10	1.78	1.78	.250	1.78	1.78	.300	2.00	2.00	2.00
57	15		4.20	1.705	1.705	.232	1.70	1.70	.282	1.915	1.915	1.915
11	0	0		4.30	1.63	.212	1.63	1.63	.262	1.84	1.84	1.84
3	15		4.40	1.56	1.56	.193	1.55	1.55	.243	1.75	1.75	1.75
6	45		4.50	1.495	1.495	.175	1.47	1.47	.223	1.66	1.66	1.66
10	0		4.60	1.405	1.405	.148	1.40	1.40	.201	1.58	1.58	1.58
13	30		4.70	1.325	1.325	.122	1.33	1.33	.176	1.50	1.50	1.50
17	0		4.80	1.255	1.255	.098	1.26	1.26	.149	1.42	1.42	1.42
21	30		4.90	1.19	1.19	.075	1.18	1.18	.122	1.33	1.33	1.33
25	45		5.00	1.11	1.11	.045	1.11	1.11	.095	1.245	1.245	1.245
30	30		5.10	1.035	1.035	.015	1.03	1.03	.068	1.17	1.17	1.17
35	0		5.20	0.96	0.96	.T.982	0.965	0.965	.037	1.09	1.08	1.08
40	0		7.30	0.89	0.89	.949	0.89	0.89	.000	1.00	1.005	1.005
46	0		5.40	0.805	0.805	.906	0.815	0.815	.T.939	0.91	0.915	0.915
52	15		5.50	0.73	0.73	.863	0.74	0.74	.917	0.825	0.835	0.835
12	0	0		5.60	0.67	.826	0.66	0.66	.872	0.745	0.745	0.745
7	45		5.70	0.595	0.595	.775	0.59	0.59	.820	0.66	0.66	0.66
16	30		5.80	0.51	0.51	.708	0.515	0.515	.763	0.58	0.58	0.58
26	45		5.90	—	—	—	—	—	.694	0.495	0.495	0.495

 $\log_{10} e \times 10^3 \times k = 6.54 \text{ min.}^{-1}$ $\log_{10} e \times 10^3 \times k = 6.56 \text{ min.}^{-1}$

data are treated in the usual way using the values 6.48 and 6.50 for the end-point. It will be observed that the values obtained for k differ from each other by 2.3 per cent. In Table II. the same data are treated by the new method using for τ the periods $1\frac{1}{2}$ hours and 2 hours; the two values obtained for k agree to within 0.3 per cent. The values of k given in the tables were obtained by plotting $\log_{10}(v_{\infty}-v)$ and $\log_{10}(v'-v)$ against t on a large scale. In every case a good straight line was obtained with no visible trend. As a small scale reproduction of the plots would be of no interest, we give instead, in the columns headed $(v_{\infty}-v)$ calc. and $(v'-v)$ calc. the values corresponding to the straight lines of our plots.

Incidentally the end-point is probably obtained most accurately by intrapolation between the two assumed end-points using the value for k obtained by the new method. We thus find $v=6.487\pm.002$.

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XLVII. *The Basis of Acoustic Measurements by Reverberation Methods.* By A. H. DAVIS, D.Sc., Physics Department, The National Physical Laboratory*.

ABSTRACT

FOLLOWING a short account of the derivation of the theoretical equations of reverberation, and a resumé of the experimental laws established by W. C. Sabine, the physical phenomena involved in reverberation measurements are discussed. Conclusions are drawn as to the conditions under which measurements may be made.

The measurement of transmission through partitions by reverberation methods is also discussed, both for the case where the transmitted sound is observed just after passing through the partition, and for a modification in which it is studied in a reverberant condition in a large room.

INTRODUCTION.

IN connexion with the design of chambers for the test, by reverberation methods, of the acoustic properties of materials and of sound sources, a short account is available¹ of the construction of the laboratory designed by Sabine for this purpose. Information concerning the basis of the work

* Communicated by the Author.

is, however, somewhat scattered, and the present paper sets out a short critical survey of the theoretical and experimental considerations upon which reverberation tests are based, and the conditions under which measurements may be made.

When a source of sound is started in a room, it gradually fills the room with sound of increasing intensity until the increasing absorption of sound energy by the walls just balances the emission of the source, and a steady state is established. The general intensity of this steady state depends upon the strength of the source and of the absorbing power of the room. Owing to interference phenomena, there is a complicated distribution of maxima and minima of sound throughout the space, and this makes it difficult to assess the average acoustical energy in this steady state. Sabine, however, established that it could be assessed from the duration of audibility of the sound within the room after the source has ceased. Naturally, the sound dies away in "waves" due to shifting of the interference system; but the ear is able to ignore these fluctuations by concentrating upon averages over finite short intervals, and so gives a measure of the duration of audibility largely unaffected by the interference phenomena. The evidence for this will be considered later. Sabine also established that the intensity so assessed depended in a simple manner upon the strength of the source and upon the absorbing power of the room. He was thus led to use the method in measuring on the one hand the absorbing power of material, and on the other the rate at which sound entered through a small test partition into an otherwise soundproof room.

THEORY.

Theories correlating the duration of audibility with the strength of the source and the nature of the room have been given by W. C. Sabine², Jaeger³ and Buckingham⁴. In all cases it is recognized that a sound suffers some two or three hundred reflexions before it finally dies away, and, in consequence, it is assumed that through random arrangement the sound-energy rapidly becomes uniformly distributed throughout the enclosure. Interference phenomena are ignored, and so results are only valid to the extent to which this is justifiable.

Jaeger's analysis may be summarized as follows:—Sound-waves from a simple source of musical sound in an enclosed space proceed outwards and suffer reflexion, diffraction, and absorption at the various enclosing surfaces. If for a

ray of sound the mean number of incidences upon the surfaces is n per second, and if the mean absorption-coefficient (or ratio of absorbed to incident energy) of the surfaces is a , and if the mean intensity (energy per unit volume) in the room at a given instant is I , then the change of intensity by absorption at the surfaces in a time dt is $dI = -I.a.n.dt$.

By a statistical method it is shown that for a ray of sound in a closed room the mean number of reflexions per second is given by $n = vS/4V$, where

V = total volume of room,

S = total surface of room,

v = velocity of sound.

If E denote the rate of emission of energy from the source, the total rate of change in unit volume of the room is given by

$$dI/dt = E/V - vaSI/4V. \quad . \quad . \quad . \quad (1)$$

This is the fundamental differential equation in reverberation work.

Buckingham's treatment is slightly different. He assumes that the sound-energy is divided up into a large number of equal parts, and that in the steady state these energy units are uniformly distributed throughout the room both with regard to position and direction of motion*. Each is assumed to move with the velocity of sound. He shows that when the intensity in the room is I (*i. e.* I energy units per unit volume) the number reaching any element of boundary surface dS in unit time is $\frac{1}{4} v.dS.I$. On incidence a fraction $\frac{1}{4} a.v.dS.I$ is absorbed or transmitted and the remainder reflected back into the room. By writing $\int_0^S a dS = aS$, the differential equation (1) is obtained, as before, to represent the rate of loss of sound from the room.

The following solutions of equation (1) relate to special circumstances stated:—

(1) Uniform sound-emission beginning at zero time:

$$I = \frac{4E}{vaS} (1 - e^{-vaSt/4V}). \quad . \quad . \quad . \quad (2)$$

(2) Steady state reached by uniform emission:

$$I_{\max.} = \frac{4E}{vaS}. \quad . \quad . \quad . \quad (3)$$

* Before establishing his formula, Buckingham discusses the acoustical condition of the air in a closed room rather fully.

(3) Emission stopped in steady state (Sabine reverberation case).

$$I = I_{\max} e^{-vaSt/4V} = \frac{4E}{vaS} e^{-vaSt/4V}. \quad . \quad . \quad . \quad (4)$$

Sabine expressed much of his work in terms of the time taken for a sound to die away to the threshold of audibility, and adopted as his standard initial condition an average intensity $I_{\max}$ equal to one million times the threshold value. In this case

$$10^{-6} = e^{-vaSt/4V},$$

whence, on putting $t=T$ for this standard condition, we have

$$T = \frac{55.2V}{vaS}.$$

This becomes

$$T = 0.05V/aS \text{ in feet units,} \quad . \quad . \quad (5)$$

$$T = 0.162V/aS \text{ in metre units.} \quad . \quad (6)$$

In effect, Sabine's own theoretical treatment established (4) in the form $I = (E/VA)e^{-At}$. He also calculated that A is related to the mean free path of sound in a room by the equation $p = aV/A$. If we recognize that p has the statistical value $4V/S$ calculated by Jaeger, Sabine's equation becomes identical with (4).

SABINE'S EXPERIMENTAL WORK.

After attempts to study the decay of sound in a room by instrumental means, W. C. Sabine⁵ finally decided to measure instead the duration of audibility as perceived by the ear. In an ordinary lecture-room, irregularities in observed duration of audibility were made surprisingly small by working at night. To secure accuracy it was necessary to suspend operations on the approach of a street car within two blocks, or the passage of a train a mile distant. Concerning the accuracy of observations, Sabine states that for a certain case individual values differed from the mean of twenty observations by not more than 0.31 second in any case, and by 0.11 second on the average. The computed "probable error" of a mean of 20 observations was 0.02 second: in ten means the maximum deviation from their average value was 0.05 second. Values obtained were satisfactorily reproducible. Indeed, observations taken every

few nights for two months in the Fogg Museum Lecture Room gave values varying from 5.45 to 5.62 seconds, with a mean of 5.57 seconds, a result which was again obtained after the lapse of one, and then of three years.

EXPERIMENTAL LAWS OF REVERBERATION.

Sabine conducted a number of experiments to determine the laws of reverberation. His description of the work is historical in form, and the earlier results are not corrected for variations in the initial intensity of the sound. However, Sabine later recognizes the need for the correction, and then refers back to the earlier work.

Sabine found experimentally:—

(1) The duration of audibility of the residual sound was nearly the same in all parts of the auditorium (Steinert Hall, Boston).

(He found 2.12, 2.17, 2.23, 2.20, 2.23, 2.27, 2.20, 2.26 seconds in various parts of the hall. There was no systematic evidence of increasing audibility at greater distances from the source. The variations are within the limits of accuracy of the experiment. Numerous later experiments, carried out more accurately but with other objects in view, have confirmed the above result.)

(2) The duration of audibility was nearly independent of the position of the source.

(3) The efficiency of an absorbent was, under ordinary circumstances, nearly independent of its position.

(4) In a number of rooms the relation between reverberation T and introduced absorbent X was hyperbolic in form, such that $(X + C)T = k$, where k was a constant for a given initial intensity, and the constant C presumably represented the initial absorbing power (aS) of the room.

(5) The absorbing powers of various arrangements of certain cushions were proportional to the areas exposed. The absorbing power of an open window was proportional to the aperture area.

(6) The constant k was proportional to the volume of the room (range studied—65 cu.m. to 9300 cu.m.). When reduced to standard initial intensity the value of k is given by

$$k = 0.164V, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whence in open-window units,

$$T = \frac{0.164V}{aS} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

(7) As expected, the decay of sound in a room was exponential in form. It was related to the absorbing power aS of the room—as determined in open-window units from the hyperbolic law—in a manner which agreed with theoretical considerations.

This work on the rate of decay of sound is described in greater detail below.

THE RATE OF DECAY OF SOUND IN A ROOM.

In the study of the rate of decay of sound in the room, Sabine employed his "multiple organ-pipe" experiment. Note was made of the duration t , of audibility in a room when a certain source was used, and of the duration t_n when a combination of sources having n times the activity was employed. It follows from (4) that a relation should be obtained of the form

$$\log n = A(t_n - t_1), \quad . \quad . \quad . \quad . \quad (9)$$

where A , defined by Sabine as the rate of decay of sound in the room, has the value $vaS/4V$ according to Jaeger's theory.

Sabine first verified experimentally that such a logarithmic relation was satisfactory, and from his results he determined A .

The actual experiments were carried out first with one organ-pipe, and then with 4 (or 16) similar pipes, each with its own wind-chest, sounded simultaneously. Provided there was no mutual action between the pipes, the emission in the latter case was four times that in the former.

As regards the technique of the experiment, one, two, three, and four pipes were used. The two- and three-pipe tests were made with various combinations, and so presumably eliminated any interference arising from the position of a given pipe.

Sabine also states that in a certain experiment he used four organ-pipes at a minimum distance apart of 5 metres, because, if placed near each other, four pipes sounded together do not emit four times the sound emitted by one. Such separation is stated to be particularly necessary for large pipes and low tones: much less separation would suffice for the higher tones.

Having determined A , Sabine then investigated its relation to the absorbing power of the room as obtained in open-window units from the hyperbolic law. On the assumption that the absorption of sound in a room takes

place on reflexion at the various surfaces, Sabine expected a relation of the form $A = (v/pS)aS$, where p is the mean free path in the room. From a variant of this equation Sabine determined the value of p for two rooms, and found them to be reasonable and to be proportional to the linear dimensions of the rooms.

With further reference to the absorbing power of a room, Sabine states that practically no damping arises from viscosity of the air. He quotes experiments conducted in two very similar rooms, bare and unfurnished, with walls of very small absorbing power and differing 35 fold in size. The absorbing power was found to be accurately proportional to areas. He states if the air-damping were even one fiftieth of the surface damping, the effect would have been noticeable.

DISCUSSION OF THE LAWS OF REVERBERATION.

Sabine's experimental propositions lead to the following deductions:—

(1) Since the duration of audibility is practically the same in all parts of the auditorium, we may infer that reverberant sound is uniformly distributed throughout the space, and that the threshold sensitivity of the ear is sensibly independent of whether it was initially subjected to the loudness of an antinode or of a node. Presumably, however, fatigue of the ear would become important with extremely rapid decay of sound.

(2) Since the duration of audibility was nearly independent of the position of the source, we may infer uniform mixing of the reverberant sound, and also that the same amount of energy was emitted by the source in the various positions. This is important because the proximity of objects and walls can affect the output from a source to some extent by tending to put the air near the source in phase or out of phase with the issuing disturbance. Indeed, Sabine⁶ quotes a case where the output of a source was considerably affected by alteration of the interference system in the room.

Reaction upon the source would be specially pronounced when the frequency concerned is near one of the resonant frequencies of the air of the room or of one of the walls etc. The author observed a case in which the pitch of a note emitted by a loudspeaker was ultimately sharpened by about 0.05 per cent., and thus brought into unison with a natural frequency of the room: the struggle lasted several

seconds. While it may not be absolutely necessary to avoid frequencies of resonance in reverberation work, it appears desirable to do so. Regions of marked resonance are always narrow in the frequency range.

(3) Since the efficiency of an absorbent was, under ordinary circumstances, nearly independent of its position, we may infer uniformity of mixing of the sound, equal incidence upon all parts of the boundary of the room, and that the output from the source was not affected by change in the interference pattern of the room resulting from the introduction of the material.

(4) That the relation between duration of reverberation and introduced absorbent was hyperbolic in form agrees with equations (5) and (6), which were based upon assumptions of uniform mixing of sound, both as regards position and direction, of constancy of absorbing power for various intensities of incident sound, and of constant emission from the source.

(5) That the absorbing powers of various arrangements of material or of open window were proportional to the areas exposed has the same implications as (4). It is well, however, to face the difficulty that—on the ordinary hydrodynamical theory of sound—when an aperture is small compared with the wave-length of the sound concerned, it does not transmit the same amount of energy as that crossing an equal area in the primary waves.

For a circular aperture about 82 per cent. is transmitted, but for a long narrow slit whose breadth is small compared with the wave-length the energy transmitted may even considerably exceed that corresponding to an equal area of wave-front in the primary waves. It is important, therefore, for correct absolute results that areas be not small compared with the wave-length. Indeed, P. E. Sabine⁷, working more recently than W. C. Sabine under the improved conditions afforded by the Wallace Clement Sabine Laboratory, has found that when the dimensions of a highly absorbent sample are not great compared with the wave-length of the sound, then the apparent absorbing power per unit area is a function of the area of the sample, of its shape, and also of its location relative to other absorbing surfaces. Measurements were made with areas ranging from 0.14 to 10.0 square metres. For felt, at the frequency for which its absorption is a maximum, namely 1024 d.v., the absorbing power per unit area decreased with increasing area, the ratio in extreme cases being about 3 to 1. At other frequencies the variations were not so great. Long

narrow shapes with an area of 3.3 square metres showed an absorbing power some 50 per cent. greater than an equal area in the form of a square.

P. E. Sabine also measured the passage of sound through rectangular openings, similar in shape, but varying in size from 0.34 to 2.8 square metres. The effect observed was the same as in the case of absorption by felt. For example, the relative transmissions of C_4 (512) per unit area through the smallest and the largest openings were in the ratio 11:8.

The results obviously suggest some qualifications in the definition of sound-absorption coefficients. Even if a number of materials of equal small area were compared, true relative values of absorption-coefficients would not be obtained: there would be a correction factor depending upon the coefficient observed and due to the difference between the absorbing power of the material and the absorbing power of the wall in the neighbourhood of the sample.

Another point also arises here. If very large samples are used, it may well prove that with very absorbent materials the assumed uniformity of mixing of reverberant sound throughout the room may be affected, unless the total area of the surfaces of the room is large compared with the area of the sample. The need for very large rooms is thus clear. Information as to the minimum size necessary is not available.

(6) That the constant k is proportional to the volume of the room agrees with the theory indicated. The correspondence between Sabine's experimental result $k/V = 0.164$ and the theoretical value 0.162 deducible from equation (6) is most striking. It implies—if everything else is satisfactory—that Sabine's open-window standard had an absorption-coefficient which was almost exactly unity on the absolute scale. Indeed, it is probable that if this had not been the case, Sabine would have found absorbing power not to be proportional to window aperture.

(7) That the decay of sound was logarithmic in form agrees with equation (4). This equation assumes the absorbing power of the room to be independent of the intensity of sound within it. Departure from the law would be expected if the ear were seriously affected by the interference phenomena, or if the threshold sensitivity of the ear depended markedly upon the initial intensity in the room. Sabine's experiments have been repeated over a vastly wider range with loudspeaker apparatus which avoids using simultaneously a number of different sources which may

react upon one another. No departure from the logarithmic law has been observed.

By conducting experiments with two different initial intensities of sound of known ratio, the actual sensitivity of the observer's ear is eliminated.

Summarizing the points raised, it appears that in reverberation measurements of absorbing power the dimensions of the sample should be large compared with the wavelength of sound, and small compared with the dimensions of the room. Large rooms are thus indicated. To average out any lack of uniformity of distribution of sound within the room, the positions of source, material, and observer should be varied: satisfactory rooms should show little dependence upon position. Particularly for frequencies near resonant frequencies of the air of the room or of any of the walls, reaction upon the source may affect its output: the proximity of other sources emitting at the same time may also affect output. It is thus desirable, to avoid resonant frequencies, to use a single source, and in each position to vary its output in a known manner. The source should be of a type which is affected as little as possible by reaction effects. Large rotating reflectors in the room would tend to average out errors due to lack of uniformity of sound within the room, due to reaction upon the source, or due to any effect the interference fluctuations may have on the ear during the decay of sound. By conducting all experiments with at least two different intensities of initial sound—of known ratio—the characteristics of the ear are largely eliminated.

APPLICATION OF REVERBERATION METHODS TO TRANSMISSION MEASUREMENTS.

W. C. Sabine⁸ also applied a reverberation method to measuring the transmission of sound through partitions. Before discussing the method, we may note that transmission of sound through partitions may take place by a variety of agencies. The sound may pass through cracks or pores in the panel, it may be transmitted by true sound-waves set up in the material of the panel by incident aerial sounds, or by the panel vibrating as a whole like a diaphragm and thus communicating the vibrations to the air on the other side. For solid panels the true acoustical transmission must usually be negligible owing to the great difference in density between the air and the panel, and the main transmission is by means of vibrations as a whole.

A vibrating panel will have certain natural frequencies at which it will respond and transmit sound more freely. In any transmission tests it is thus desirable to use pure tones, and to cover a range of pitch. The resonant frequency will depend upon the size of the panel and upon its method of fixing, so that, while information concerning transmission at resonance for particular panels may be of value, figures obtained away from resonance regions will be of more general application.

In W. C. Sabine's reverberation method of measuring transmission, the partitions were built into an aperture in the double wall between two adjacent but structurally separate rooms. Broadly the method consisted in producing, by means of a source in the larger room, a volume of sound of which the intensity in terms of threshold audibility was known, and then, by stopping the source, allowing the sound to decay at the rate natural to the room until it ceased to be audible on the other side of the partition. The intensity of the sound at this instant was estimated from reverberation measurements in the source room, and was taken to be numerically equal to the coefficient of transmission of the partition. In later work carried out in the specially designed Wallace Clement Sabine Laboratory of Acoustics, P. E. Sabine determined simultaneously the duration, after the source had ceased, of the residual sound in the source chamber and in the adjacent test chamber, and computed from these results the ratio of intensity on the two sides of the partition.

It is clear that, to obtain a simple transmission-coefficient directly from such experiments, the receiving-chamber must have absorbent walls in order to ensure that the entering sound is heard alone, without any enhancement arising from reflexions and reverberation. The listener in this case should be situated close to the panel, for there the entrant sound has not been enfeebled by spreading. P. E. Sabine⁹ observed experimentally that the acoustic condition of the room does affect the values of apparent transmission, and that the effect was least pronounced when observations were confined to positions near the transmitting panel. He adopted this position as his normal procedure.

In such tests the duration of audibility is not heard under precisely the same conditions in the two rooms. In the source-room the sound-energy is moving to and fro in all directions; in the receiving-room it has a general inward direction. It seems unlikely that the ear would differentiate, but experiment alone can decide this.

The author¹⁰ recently derived equations for the decay of the reverberant sound in each of two adjacent rooms as used for transmission tests, when the receiving-room is not completely absorbent. These indicate how the reverberant sound in the second room depends upon its acoustic condition, and that the reverberant sound may be appreciable in comparison with the undiffused entrant sound.

The equations, however, also suggest an alternative method of measuring transmission: namely, by making both rooms reverberant and listening in the receiving-room to the diffused reverberant sound rather than to the sound near the panel which is just entering the room. While the general equations are complicated, they are greatly simplified if the transmittance through the panel be small, and become very simple if the source-room be sufficiently more reverberant than the receiving-chamber.

Simultaneously Buckingham¹¹ published equations for the case of low transmittance, which correspond exactly with a special case of the equations referred to above. While he expresses a preference for equal rooms—which also give simple relations,—he recommends for accuracy that, if the two chambers are not equally reverberant, one should be markedly less reverberant than the other.

Buckingham suggests, however, that the more reverberant one should be used as the receiving-chamber, on the ground that for a given activity of source the duration of audibility in it will otherwise be too short for accurate observation. However, there is a somewhat remarkable reciprocal property of symmetrical partitions, deducible from even the most general relations, that the reverberant sound in a room A due to a source in a room B is identical with that in the room B due to a source of the same activity in A. The argument, on the basis of longer audibility, to use the larger room as the receiving-room is thus untenable. On the other hand, as regards duration of audibility in the source-room, it is found to be best to have the source-room the more reverberant—the case studied in my earlier paper.

This latter arrangement of markedly different rooms also gives simpler equations in that the rates of decay in the two rooms are the same, whereas if the receiving-room be the more reverberant, the two rates of decay would be different and the experimental procedure would probably be more involved.

In some conditions, however, equations given for reverberant sound in the receiving-room may not represent the sound actually heard at special points (such as near the

panel), owing to the sound which is proceeding direct from the panel and which has not yet been generally diffused by reflexion. When the source-room is the more reverberant, the entrant sound can be made to die away at the same rate as the reverberant sound—a possible simplification. If, however, the receiving-room be the more reverberant, the entrant sound would die away at a greater rate than the reverberant sound, and undoubtedly it could be arranged to decay so rapidly that an ear in the receiving-chamber would ultimately be listening only to the decay of sound which had been well diffused by repeated reflexions, and which obeyed the reverberation equations.

If this early suppression of the entrant sound be vital for reverberation work—one can hardly say without experiments,—the advantages associated with a more reverberant source-room or with equally reverberant rooms would have to be sacrificed.

Apart from these special points in transmission measurements, the general conditions necessary for reverberation work need to be fulfilled. Large rotating reflectors in the source-room are especially necessary in order that, in spite of interference phenomena, the average intensity of sound against the partition in a series of observations should be equal to the average in the room. It was apparently for this reason that W. C. Sabine introduced rotating reflectors. He also enclosed the observer's seat in a box, so that the condition of the room was rendered independent of the presence or absence of the observer. Any resonance frequency of the connected rooms should be avoided, for the information obtained might express the peculiarity of the laboratory rather than a property of the panel.

As Buckingham points out, in the source-room the absorptivity of a feebly-transmitting partition will not usually be very different from that of the remainder of the walls, and the presence of the panel will not cause any serious departure from the uniformity of energy distribution assumed in the theory. However, in the receiving-room the panel alone is acting as source, and the uniformity of distribution will be improved if the area of the walls of this room be large in comparison with the area of the panel.

For panels of high transmittance, however, the area which is a source of sound for one room is a sink of sound for the other, and both rooms must be large.

Summarizing the position with respect to transmission measurements, conditions in the source-room must generally satisfy the requirements set out previously in connexion

with absorption measurements. In particular, rotating reflectors or some equivalent appear desirable. If highly-transmissive—or very absorbent—panels are tested, the source-room will need to be large in comparison with the area of the test partition, but for ordinary hard and moderately sound-proof partitions this requirement is less pronounced.

If the receiving-room is used after the manner described by Sabine, it should have absorbent walls and be non-reverberant. It may be small.

If the receiving-room is reverberant and attention is directed to the reverberant sound within, the room must be large in comparison with the area of the test panel. Simplest relations are obtained if it is less reverberant than the source-room; but to ensure early suppression of the sound entering the receiving-room, it may be necessary to make the receiving room the more reverberant.

February 1926.

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XLVIII. *On the Effect of the Shape of the Cathode on the Glow Discharge.* By W. STEPHENSON, M.Sc., *Armstrong College, Newcastle-on-Tyne* *.

INTRODUCTION.

THE effect of the shape of the cathode on the current, Crookes's Dark Space (C.D.S.) thickness, and cathode fall of potential of the glow discharge, has received attention by Aston † and others, and recently by Gunther-Schulze ‡

* Communicated by Prof. Geo. W. Todd, M.A., D.Sc.

† F. W. Aston, *Proc. Roy. Soc. A*, lxxxvii. p. 428 (1912).

‡ A. Gunther-Schulze, *Zeit. für Physik*, xix. p. 313 (1923).

and Prof. M. E. Hufford *. Gunther-Schulze experimented upon a current-increasing effect that occurs under certain circumstances between equipotential cathode surfaces; Hufford upon phenomena at a hole in a cathode, and discharge between equipotential cathodes. The object of this paper is to describe a current-increasing and cathode fall of potential decreasing effect, thereby serving as an introduction to the general effect touched upon in various aspects by the above workers.

General features of the work can best be stated here. The glow discharges are free from positive column, so that the voltage across the discharge-tube terminals is nearly the same as the fall of potential between the cathode and the boundary of the C.D.S. and the negative glow. The glass vessels containing the electrodes were large compared with the size of the electrodes; and air, dried by phosphorus pentoxide, was the gas through which the discharge was passed. The voltage supply was the 480 d.c. city mains, dry batteries, and an "Anode Converter" which provided about 500 volts.

I. EXPERIMENTS WITH COMPOUND CATHODES.

Some striking phenomena occur when the usual simple cathode is replaced by a variety of slightly complex cathodes, and with compound cathodes, two disturbances of the uniformity of the glow discharge are illustrated:—

(i.) A current-increasing effect, evinced by an increased brightness of the negative glow, measurements of current density, and reduction in the thickness of the C.D.S.

(ii.) A reduction in the cathode fall of potential, evinced in part by a decrease in the total voltage across the discharge-tube terminals, and in part by the appearance of the negative glow under "normal" conditions (when the voltage across the discharge tube remains constant at a minimum value, and the current density is maintained at a constant value by self-adjustment of the available cathode area utilized in the discharge).

Two Parallel Wires as Cathode.

A discharge tube was constructed in which three co-planar parallel aluminium wires A, B, and C, each 5 cm. long, 1 cm. apart, were used as electrodes. A was used as anode, and B and C together served as cathode. At pressures in air of the order 1 mm. Hg, in the "abnormal" current conditions

* M. E. Hufford, *Phil. Mag.* vol. 1. p. 1197 (1925).

both B and C are surrounded by a uniform cylindrical negative glow, the radial C.D.S. thickness being the same for B as for C. The equations

$$p.d_n = \text{constant}, \dots \dots \dots (1)$$

$$\frac{I_n}{p^2} = \text{constant}, \dots \dots \dots (2)$$

give the approximate relations between the "normal" C.D.S. thickness (d_n), the "normal" current density (I_n), and the pressure (p).

At lower pressures, when the "normal" thickness of the C.D.S. for a particular pressure becomes greater than half the distance between the wires B and C, the uniformity of the negative glow is destroyed, and the space immediately between B and C shows a brighter glow, and a smaller C.D.S. thickness, and therefore a greater current density, than the space to the left and right of the two wires. This superior brightness persists under the "normal" discharge conditions. At a lower pressure, the bright parts become separated, and discharge does not pass in the straight line joining B and C. In this case the negative glow for the "normal" condition consists of only the bright part of the glow, lying between, but above and below, B and C. This suggests that the "normal" cathode fall of potential for the bright part of the glow is less than that for the glow to the left and right of B and C under the same pressure conditions.

A Spherical Spiral Cathode.

A further degree of the same effect is shown in the glow discharge of a point anode at the centre of a spirally wound spherical cathode. An anode wire, 1 mm. diameter, was covered with glass tube to within 3 mm. of its end and was placed at the centre of a sphere, made in spiral form from the same wire.

The usual discharge characteristics were obtained at pressures of the order 1 mm. Hg, and equations (1) and (2) obtain. At low pressures the effect occurs that is described above for the cathode of two parallel wires; and at a pressure depending upon the distance apart of the adjacent rings that constitute the spiral sphere, the "normal" negative glow consists of only a continuous bright spiral lying between the adjacent wires of the spiral. At still lower pressures, when the C.D.S. thickness becomes of the order of the distance between the adjacent rings, there are two distinct parts of the negative glow:—an inner sphere of negative glow,

concentric with the cathode, and brighter than the other, and an outer sphere of negative glow. At pressure 0.05 mm. Hg, the outer C.D.S. may have a thickness of 2 cm., while at the same time the inner C.D.S. is only 0.5 cm. thick. Under such circumstances the "normal" discharge condition is characterized by complete absence of the outer negative glow, and only the inner face of the sphere is utilized in the discharge. There are thus two effective conditions at this cathode:—

(A) The current-increasing effect of the concave cathode surface of the sphere.

(B) A current-increasing effect of the same nature as that described in the case of the two parallel wires.

Both are accompanied by a decrease in the cathode fall of potential.

Of particular interest is a bright "bead" of glow that was situated in the centre of the first spiral of one of the spherical spiral cathodes that was used. The first spiral left, as it were, a hole in the cathode surface that was wider than the distance between the adjacent rings of the cathode. At these low pressures this cathode acted in the same way as did the cathodes used by Hufford*. The bright "bead" increased in length, and decreased in thickness, for decrease in the total current through the discharge tube; it was, under all conditions of current, brighter than any other part of the negative glow, and was brighter the greater the current through the tube. These characteristics suggest that the "bead" is of the nature of the usual negative glow, resulting as a combination of the two current-increasing conditions (A) and (B); but the round bead-like end was always turned away from the anode, and under certain conditions its colour suggests that it is of the nature of a positive column striation.

Concentric Cylindrical Spirals as Cathode.

The two effects (A) and (B) are shown in a cathode consisting of two concentric cylindrical spirals that are used together as cathode, the anode being a straight wire passing down the axis of the cylinders. Such a discharge tube was made of 2 mm. diameter iron wire, the cylinders being 4.5 and 2.5 cm. diameter respectively.

Using the inner cylinder alone as cathode and the central

* *Loc. cit.* p. 1197.

wire as anode, the phenomenon occurs that is indicated above for the spherical cathode. When both cylinders are used together as cathode the effect of the opposing cathode surfaces (B) is greater, at a suitable pressure and current, than the effect (A) due to the curvature of the cathode. After passing through the stages corresponding to those for high pressures for the spherical cathode, the condition is reached at which the "abnormal" currents are represented by three negative glows. First, there is a cylindrical negative glow surrounding and co-axial with the outer cylindrical spiral; secondly, a much brighter negative glow in the annular space between the two cylinders; thirdly, a negative glow that is not so bright as the second, but brighter than the first, situated in the inside of, and co-axial with the inner cylinder. Under pressure conditions that depend upon the dimensions of the cylinders, the annular negative glow is easily the brightest of the three, and in such a case, as the current through the tube is reduced, the outermost glow disappears first, then the innermost follows, and the "normal" condition is represented by only the annular negative glow. Since the curvature is greater for the inner cylinder than for the outer one, the current-increasing effect due to curvature should be less for the annular space than for the innermost space between the anode and the inner cylinder. In the above case the current density is greater in the annular space than in the space between the anode and the inner cylinder. Thus the very bright annular glow indicates a current-increasing and cathode fall of potential decreasing effect due to the opposing surfaces offered by the inside of the outer and the outside of the inner cylinder. The effect due to a concave cylindrical cathode surface is a particular case of the general effect due to two opposing cathode surfaces.

At the time of writing this paper, Hermann Schüler* gives, in the January 9th number of the *Zeit. für Physik*, some interesting results and uses of the inner glow to a cylindrical cathode.

II. THE DISCHARGE BETWEEN EQUIPOTENTIAL PLATES.

The U-shaped Cathode.

Quantitative work is possible with discharge tubes of the above types, but a U-shaped cathode and electrode disposition of the kind used first by Gunther-Schulze simplifies

* Hermann Schüler, *Zeit. für Physik*, xxxv. p. 323 (Jan. 1926).

description and facilitates measurement of, and more clearly exemplifies, the current-increasing effect, while at the same time making possible a ready comparison between current conditions to a plane cathode and a cathode consisting of two equipotential parallel plates. For a detailed account of the discharge to a U-shaped cathode one is referred to the work by Gunther-Schulze* on the effect of the shape of the cathode on the current of the glow discharge in hydrogen. The following experiments illustrate the work that is possible with a U-shaped cathode in air.

Two exactly similar strips of brass, approximately $6.0 \times 0.85 \times 0.1$ cm., were used as electrodes, one (*k*) being bent to a U-shape, with arms 0.5 cm. apart, and the other (*I*) used flat. One could be used as anode and the other as cathode. With the *I*-electrode as cathode, the value I_n of the current through the discharge tube when the cathode is just completely covered with the negative glow (or the value when the voltage across the discharge tube terminals begins to remain at a constant "normal" value, assuming that the current is being reduced from "abnormal" to "normal" values) will give the value I_n/A for the "normal" current density, where *A* is the area of the cathode surface. Thus I_n at all pressures will give relative values of the "normal" current densities for those pressures, and if the same condition holds for the U-electrode it follows that $k_n/I_n = 1$, at each value of the pressure, assuming that the U-electrode is without effect on the current density.

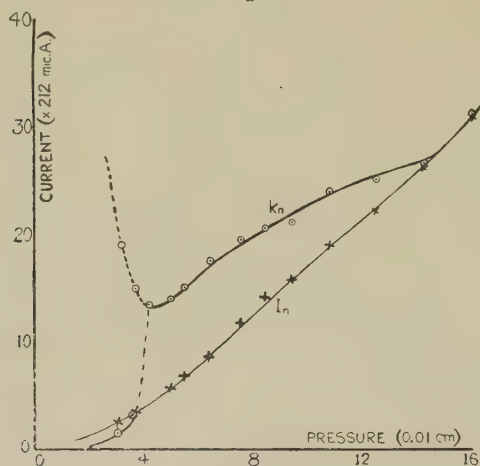
At pressures greater than 0.15 cm. Hg, the values of I_n and k_n are almost identical at a particular pressure. This equality is what is expected, since the negative glows in each case are exactly similar. For very much greater pressures, when the negative glow closely wraps the cathode, the current k_n becomes less than I_n at the same pressure. The current to the inside of the U-shape encounters a higher resistance in the narrow slit of the U than it does for the *I*-electrode.

The graph, fig. 1, shows experimental results obtained for I_n and k_n over the pressure range 0.16 to 0.02 cm. Hg. Fig. 2 gives the ratio k_n/I_n for a similar set of readings. It is seen that k_n is always greater than the corresponding value of I_n . The negative glow for the U-electrode as cathode is now as shown in fig. 3, a sketch of the glows at

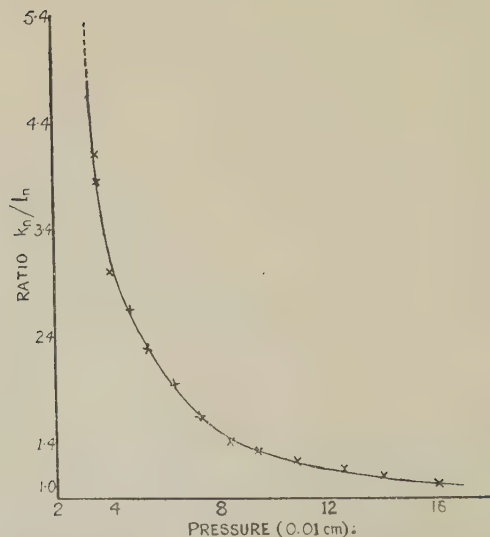
* Gunther-Schulze, *loc. cit.*

$p=0.06$ cm. Hg, the current being "abnormal." There are two parts of the negative glow :—

Fig. 1.



Fi 2.

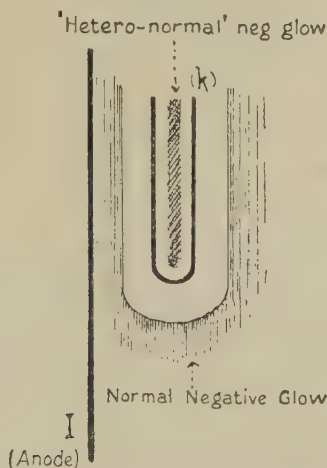


(1) An outer glow, with C.D.S. thickness the same as is obtained for the I -electrode as cathode, at the same pressure and current density conditions.

(2) An inner negative glow, more brilliant and clearly

defined than the outer one, and with a smaller C.D.S. thickness: the current density to the inside is therefore greater than that to the outside at the same pressure. The "normal" condition is represented by complete absence of the outer glow, and the various "normal" currents are accommodated by only part of the opposite faces of the inside of the U being utilized in discharge. As is shown in fig. 1, the "normal" current density to the inside of the U is much greater than the "normal" value that is expected from equation (2). At the same time the voltage across the discharge tube is less than the "normal" value for the particular pressure, for discharge to the I-electrode as cathode. The increase in k_n begins as soon as the "normal"

Fig. 3.



C.D.S. thickness for the outside of the U becomes greater than about half the distance between the opposite arms of the U, as is shown in Table I.

At pressures less than 0.02 cm. Hg, k_n is generally less than I_n at the same pressure. The C.D.S. thickness for these pressures is too great to allow entry of the discharge to the inside of the U, and only the outside is utilized in the discharge.

From the experiments it appears that the ratio k_n/I_n reaches a maximum near the pressure 0.03 cm., and then rapidly decreases until, at $p=0.02$, the ratio is less than 1. The decreasing values of the current, however, are obtained under different temperature conditions, and for this reason it is difficult to determine the course of the curve near the

pressure 0.03 cm. Hg. At such pressures the current could be one of two values, under the same external circuit and pressure conditions. At $p=0.032$ cm. Hg, k_n was 425 or 3028 micro-amperes. The second value existed until the inner space became so hot that discharge between the opposing arms of the U was impossible, and the current dropped to the low value. At the large current densities

TABLE I.

Pressure. cms. Hg.	C.D.S. thickness for inside the U.	C.D.S. thickness for outside the U.	k_n .	I_n 2	Current to inside of the U. ($k_n - I_n/2$)	Voltage across terminals.
0.124	0.22 cm.	0.22 cm.	24.8	10.6	14.2	316
0.11	0.23	0.26	23.8	9.7	14.2	311
0.096	0.22	0.29	22.8	8.6	14.2	318
0.085	0.22	0.33	21.4	7.8	13.8	321
0.074	0.22	0.34	19.8	6.2	13.6	326
0.065	0.22	0.39	18.0	5.1	12.9	328
0.057	0.22	0.43	16.0	3.9	12.1	345
0.049	0.22	0.46	—	—	—	—
0.043	0.22	0.48	12.6	1.9	10.7	385
0.034	0.22	0.52	—	—	—	—
0.031	0.22	0.55]	20.0	1.0	19.0	405

Distance between arms of U-shape 0.5 cm.

the voltage across the tube increased, as is shown in Table I., but the voltages were still very much less (100 volts or so) than those obtaining for the low current condition.

A summary will now be useful:—

(i.) Coincident with the very near approach of the boundaries of the C.D.S.'s of two equipotential cathode surfaces that are opposing each other, there occurs a current-increasing effect.

(ii.) The resulting large currents pass at a cathode fall of potential not greater than the cathode fall for the "normal" condition for the same pressure and cathode material, but for the discharge between a plane cathode and anode.

In other words, we have an "abnormal" current passing at the usual, or less than the usual, "normal" cathode fall of potential (whilst, generally, any increase in current above the "normal" results in an increase in voltage, according to

an equation of the type given by Aston *). These currents, and voltages, I propose to name "hetero-normal."

(iii.) The voltage increase noted in Table I. shows that the "hetero-normal" effect exists equally well as an "hetero-abnormal" effect. The following experiments will show this more clearly.

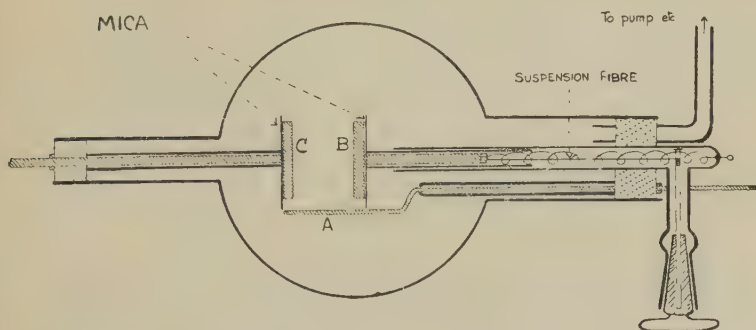
III. THE "HETERO-NORMAL" EFFECT.

For further experimentation on the "hetero-normal" effect, a discharge tube should provide :—

- (i.) means for variation of the distance between the opposing cathode surfaces ;
- (ii.) simplification of the discharge conditions, by getting rid of extraneous discharges such as that passing to the outside of the U-electrode.

A simple discharge tube that satisfies these requirements is shown in fig. 4. B and C are brass cathodes, the backs

Fig. 4.



of which are covered with thin mica. Each is 3.29 cm. diameter: leads-in are covered with glass tube, so that discharge is confined to the opposing faces of B and C; and a glass tap, with central spindle around which a supporting thread runs, affords the means for variation of the height of B above C. B was restricted to vertical movement by a sliding arrangement between two co-axial glass rods (so that the surfaces of B and C were always parallel to each other) as is indicated in the diagram. The anode was a brass rod 5 cm. long, introduced as shown. The electrodes were contained in a 2-litre flask, thus ensuring freedom from "wall" effects. Apart from "hetero-normal" measurements, we have to

* Aston, Proc. Roy. Soc. A, lxxix. p. 84 (1907).

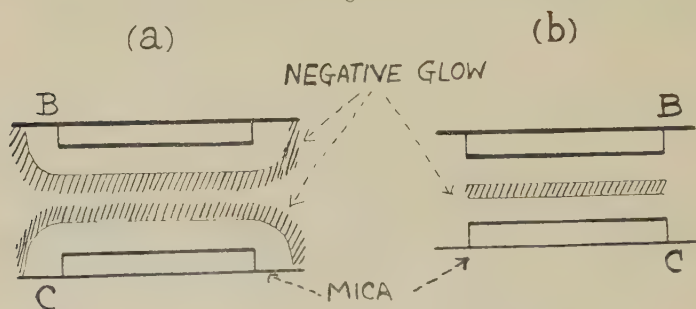
show that the current-increasing, and cathode fall of potential decreasing effect, occurs in the "hetero-abnormal" glow discharge condition.

Variation of the "Hetero-normal" Effect with Change of Distance between the opposing Cathode Surfaces.

The "hetero-normal" effect is obtained in these experiments by varying the distance between the cathode surfaces B and C (now called distance D), and maintaining the current at a value sufficient to just completely utilize the available cathode area in the glow discharge.

An important characteristic of the "hetero-normal," and "hetero-abnormal" glow discharge is illustrated in the type of negative glow that is obtained for various positions of B above C. Fig. 5 (a) shows the "normal" negative glow for

Fig. 5.



a value of D greater than about twice the "normal" thickness of the C.D.S. at the particular pressure; for D less than twice the C.D.S. thickness, the negative glow is as shown in fig. 5 (b). We see that the essential difference between the "normal" and the "hetero-normal" glow is that the latter is only obtained at the points of intersection of perpendiculars from both the opposing cathode surfaces. Thus, only the opposing faces of B and C are utilized in the "hetero-normal" or "hetero-abnormal" discharge, while the whole cathode area, the rims as well as the faces of B and C, are utilized in the "normal" or "abnormal" discharge. At any pressure, when D is less than twice the "normal" C.D.S. thickness (d_n), a "normal" discharge cannot take place between B and C. However, for any value of D it is possible for an "abnormal" discharge to pass in the space between B and C, because at some high value of the current density the distance D will be equal to

about twice an "abnormal" value (d_a) of the C.D.S. thickness. The factor that will decide whether the discharge is "abnormal" or "hetero-abnormal" is the one of the difference in cathode fall of potential, and as this experiment will show, the voltage across the terminals of the discharge tube is always less for the "hetero-normal" or "hetero-abnormal" discharge than for the "abnormal." Thus, an electron or positive ion movement that is always perpendicular to both the opposing cathode surfaces, resulting in a decrease in cathode fall of potential, is the chief characteristic of the "hetero-normal" and "hetero-abnormal" discharge.

Table II. gives representative readings of the current (in this case proportional to the current density, since the cathode area is fully utilized in the discharge in each case), the voltage across the discharge-tube terminals at that current value, and the corresponding thickness of the C.D.S. for various pressures and distances D. The table shows that

TABLE II.—Showing variation of I, V, and d , for different values of D, the available cathode area being just completely utilized in the discharge.

Pressure cm. Hg.	D cm.	d cm.	I ($162 \cdot 10^{-6}$ amp. units).	V volts.	Remarks.
0.111	2.47	0.29	77	340	"Normal" discharge.
	1.88	0.28	78	340	
	1.31	.25	73	340	"Hetero-normal" discharge.
	0.96	.28	72	339	
	0.78	.25	73	330	
	0.60	.22	78	327	" "
	0.55	.18	100	318	
	0.45	.16	133	317	
	0.40	.15	210	311	
	0.31	.12	345	305	
	0.28	.09	690	310	
	0.24	.07	1060	317	
0.078	3.0	0.34	34	336	"Normal" discharge.
	1.94	.34	34	336	
	1.48	.37	33.5	332	
	1.10	.37	34	330	
	0.94	.34	39.8	330	
	0.66	.29	64	329	"Hetero-normal."
	0.55	.21	120	330	
	0.44	.18	240	361	"Hetero-abnormal."
	0.39	.14	370	368	

TABLE II. (*continued*).

Pressure cm. Hg.	D cm.	d cm.	$\frac{1}{(163 \cdot 10^{-6} \text{ amp. units.})}$	V volts.	Remarks.
0.057	2.64	0.52	21.5	345	"Normal."
	1.84	.54	21	340	
	1.59	.54	21	340	
	1.34	.49	22	336	
	1.17	.44	26	330	"Hetero-normal."
	1.11	.36	35.5	330	
	0.87	.34	48.5	330	
	0.70	.26	76	330	
	0.58	.20	108	330	
	0.49	.17	190	345	"Hetero-abnormal."
	0.39	.14	385	380	
0.042	3.83	0.83	8.1	385	"Normal."
	3.17	.96	7.8	385	
	2.58	.90	7.8	385	
	2.23	.84	7.8	385	
	2.14	.84	8.6	385	
	1.93	.78	10.8	385	
	1.72	.67	13.0	385	
	1.6	.67	15.1	385	
	1.46	.59	18	373	"Hetero-normal."
	1.32	.51	23.5	370	
	1.22	.48	27.5	364	
	1.10	.42	35	359	
	0.99	.38	44	359	
	0.93	.36	54	355	
	0.83	.33	64.5	353	
	0.80	.30	78	353	
	0.73	.27	96	353	
	0.66	.21	138	346	
	0.53	.19	222	356	
	0.47	.17	520	377	"Hetero-abnormal."

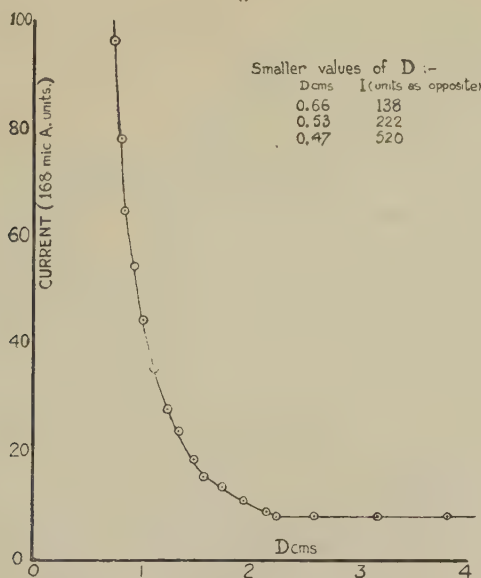
I_n , V_n , and d_n are approximately constant for the larger values of D , but that, as D decreases we have a rapid increase in the current density, together with a decrease in the voltage across the discharge-tube terminals. Graph fig. 6 shows the I - D curve for the results of Table II., at $p=0.042$ cm. Hg. The negative glows corresponding to the current increases are "hetero-normal" so long as the voltage V is less than, or equal to, V_n , the "normal" value of the voltage at that pressure. The higher voltages are generally "hetero-abnormal," due to the fact of heating at the cathode for these large currents, or because there

appears to be a minimum distance apart of the surfaces B and C for which a strictly "hetero-normal" discharge can pass, the discharges being "hetero-abnormal" for the distances smaller than this minimum.

The Volt-Ampere Characteristics.

At a particular pressure, D was maintained at various constant values, and the volt-ampere characteristics were taken as a result of varying the current passing through the discharge tube. Table III. shows typical results. For large

Fig. 6.



values of D the discharges were first "normal" and then "abnormal," and the glows are as in fig. 5 (a). For the smaller values of D, the negative glow is of the fig. 5 (b) type, and the discharge is first "hetero-normal" and subsequently "hetero-abnormal." It is seen very clearly that there is a lowering of the cathode fall of potential in the "hetero-normal" and "hetero-abnormal" discharges. The characteristics at all pressures indicate a minimum cathode fall of potential V_s for a particular value or values of D, the average decrease $(V_n - V_s)$ being 22.5 volts for one series of results over the pressure range 0.1 to 0.04 cm. Hg. At pressures lower than 0.02 cm. Hg, the size of the

cathode becomes of the same order as the thickness of the C.D.S. experimented upon, and the symmetry of the glow discharge is disturbed. The empirical equation connecting V and $\frac{1}{\sqrt{I_s}}$ is of the form given by Aston*, except that both the constants E and F are smaller in the "hetero-abnormal" than in the "abnormal" discharge.

TABLE III.—Volt-ampere characteristics for various values of D . Pressure 0.08 cm. Hg.

D cms.	I ($162 \cdot 10^{-6}$ amp. units).	V volts.	d cms.	Remarks.
15.0	27	384	.52	Full cathode area utilized. <i>i. e.</i> "abnormal" discharge. No "hetero-normal" effect.
	40.5	383	.46	
	53.5	386	.39	
	76	392	.34	
	94	396	.31	
	110	415	.30	
	230	465	.27	
	310	505	.25	
	540	560	.20	
1.14	27.5	390	—	Full cathode area utilized. No "hetero-normal" effect.
	52.5	390	.42	
	76	392	.38	
	118	415	.28	
	140	420	.26	
	260	442	.24	
	360	480	.22	
	600	540	.20	
	620	560	.19	
0.62	32.5	340	.22	Only $\frac{1}{4}$ area utilized. "Hetero-normal." Full area utilized. "Hetero-abnormal."
	63.5	343	.22	
	94	344	.22	
	117	344	.21	
	152	352	.21	
	190	361	.20	
	320	398	.17	
	475	430	.17	
0.50	31.7	342	.18	"Hetero-normal." Full area utilized. "Hetero-abnormal."
	64	342	.18	
	96	342	.18	
	111	342	.18	
	168	342	.18	
	190	342	.18	
	335	390	.16	
	495	408	.15	
	560	470	.12	

* Aston, *loc. cit.*

One matter must be referred to at this stage, because it may be thought that the voltage decreases and the current increases shown in the above characteristics are due to heating effects.

My introductory work with the compound cathodes has been added partly because the work shows the "hetero-normal" effect under conditions that cannot easily be criticised from the aspect of temperature changes, resulting in the current phenomena. Heat radiation from the cathode surfaces B and C is more difficult the nearer the two surfaces are together; and the surfaces, and the space between them, will heat up more rapidly the nearer they are together. That heating is inadequate to account for the currents can be shown in various ways. Thus at low pressures (corresponding to 0.03 cm. Hg, in the case of the experiments on the U-cathode above), the energy carried up to the cathode for a particular C.D.S. thickness is greater than that carried at a higher pressure (because the cathode fall of potential is greater for the lower pressure), and greater heating is the result. The increased heating results in a decrease in current density, and finally discharge to the space giving the "hetero-normal" effect ceases. If the electrode C is covered with a thin sheet of mica, the heating for B should be present just as for when C was used as cathode. The discharge from B, however, is "abnormal," with essentially the same characteristics as are obtained for larger values of D at the same pressure, and for C covered. If heating the cathode was affecting the discharge in any way we should not expect the clear confinement of the discharge under "hetero-abnormal" conditions to the point of intersection of perpendiculars from opposing cathode surfaces—and this can be tested very conveniently by making the electrode B to be displaced to one side with respect to C. The definite form that Aston's equations* take for the "hetero-abnormal" discharge indicate that heating effects are inappreciable except for very high current densities, a hundred times or so normal. Further, it is likely that heating the gas will result in a decrease in current density in the inner space.

The Thickness of the C.D.S.

The thickness d , as well as D , was measured on a vertically travelling microscopic stand, fitted with a sighting tube. The sharp edge of the "hetero-normal" glow made possible

* *Loc. cit.*

accurate measurements of d_s , the "hetero-normal" C.D.S. thickness, even although the maximum value of d_s was only in the neighbourhood of 1 cm. The distance from B to the nearer boundary of the C.D.S. and the negative glow was always the same as the distance C to its nearer glow boundary. Fig. 7 shows typical experimental results. The relation at all pressures is linear, *i. e.*,

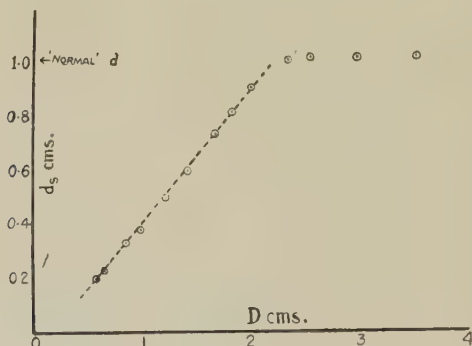
$$d = mD - r \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where m and r are constants. m appears to be the same for all pressures, and r is very nearly zero, the best experimental conditions giving

$$d_s = 0.44 D.$$

An experiment by Gunther-Schulze* suggested that the

Fig. 7.



decrease in the thickness d_s was inversely proportional to the distance between the opposing cathode surfaces: this is not incompatible with the above equation, because at the small values of D the glows were "hetero-abnormal" and not "hetero-normal."

The Variation of d_s with the Current Density.

Aston has shown that two empirical equations connect the magnitudes I , V , d , and p . In spite of the great current density differences for various values of D , and for little change in V , the equation

$$d = \frac{B}{\sqrt{I_s}} + \frac{A}{P}$$

* A. Gunther-Schulze, *Zeit. für Physik*, xix. p. 328 (1923).

is in agreement with all values of d_s and I_s in these experiments. Owing to the "hetero-normal" discharge, the constants B and A are capable of fairly accurate measurement with rough apparatus. The relation between d_s and I_s will, however, be left over for a future paper, because of the intimate connexion between the relation as obtained experimentally and that looked for on the basis of the various space-charge equations that have been applied to the discharge at the cathode.

AN EXPLANATION OF THE "HETERO-NORMAL" EFFECT.

It is recognized that the boundary of the C.D.S. and the negative glow is a region in which positive ions predominate. Thus, the recent work by Compton, Turner, and McCurdy * (in which Langmuir's † method was used for the determination of the ion concentration etc.) indicated that the electron concentration at the anode side of a particular negative glow was 101, and the positive ion concentration 51: corresponding concentrations at the middle of the same negative glow were 130 and 900 respectively. Let us assume that there is a layer of maximum concentration of positive ions near, or at, the boundary of the negative glow, and that the current through the C.D.S. is carried for the main part by positive ions. Then at any particular value of the cathode fall of potential, the total current across the C.D.S. can be increased in two ways:—(1) The positive ions at the layer of maximum concentration might be initially at rest in one case; and in the case of the current-increase might have initial velocities, thus facilitating movement of positive ions across the C.D.S. (2) Or, the region of maximum concentration of the positive ions might be moved as a whole nearer to the cathode surface. These two ways might be one and the same, and they amount to the same thing, an increase in the current carried across the C.D.S.

Now in order that the large density of ionization can be maintained at the negative glow, electrons, falling from the cathode surface region, are assumed to cause ionization by collision with the gas molecules in the negative glow region. The ions that are so produced commence life in a region of very small field intensity, and the positive ions, in particular, will not move far from their initial position of production before they are the victims of recombination. The efficiency

* Compton, Turner, & McCurdy, *Phys. Rev.* xxiv. p. 597 (1924).

† I. Langmuir, *General Elec. Rev.* 1923, p. 731.

of the electrons that produce positive ions in the negative glow region must therefore be small. If, however, an electron passing from the cathode surface penetrates the C.D.S. of an opposing cathode surface, such as we might assume in the case of the discharge between equipotential plates in the "hetero-normal" condition, the ions that are produced by collision with the gas molecules are initially in a region of strong electric field, and the positive ions will immediately begin their movement towards the cathode surface in the C.D.S. of which they are produced. These positive ions will thus not be such easy victims of recombination: the efficiency of the electrons for effective production of positive ions is therefore at a maximum when the ionization takes place in the C.D.S. An effect of this kind would explain the "hetero-normal" condition, both as regards the current increases and the cathode fall of potential decreases. The region of maximum concentration of positive ions would, in effect, be moved nearer to the cathode surface, so that it is possible for a larger number of positive ions to reach the cathode surface. Or, the required current density can be carried at a smaller cathode fall of potential because of the initial velocities of the positive ions.

In the paper mentioned above, Schüler* explains the same effect that occurs in the inside of a cylindrical cathode as a result of the "Prinzip des kleinsten Zwanges."

PHENOMENA AT A HOLE IN A CATHODE.

The "hetero-normal" effect is germane to part of the phenomena described by Prof. M. E. Hufford†. The paper gives:—(a) A study of the discharge of electricity between parallel and equipotential plates which form the cathode of a discharge tube (see Plate xxxiv., *loc. cit.*). Experiments were made with different cathode materials, gases, and sizes of hole in the cathode, and the following characteristics were reported:—(b) The presence of a "bright bead" passing through the hole. (c) A glow filling the volume between P and P'. (See fig. 1, Hufford, *loc. cit.*)

(a) Hufford's discharge tube cannot be used to examine the discharge between equipotential plates over the range of pressures giving the "hetero-normal" effect. With the opposing cathode plates 4.8 cm. apart, gas pressures giving "normal" thicknesses of the order 2.4 cm. must be obtained before the "hetero-normal" effect becomes evident, and at

* Hermann Schüler, *Zeits. für Physik*, xxv. No. 5, p. 324 (1926).

† Prof. M. E. Hufford, *Phil. Mag.* vol. 1. No. 300, p. 1197 (1925).

the required pressure it is not possible to have a discharge between P, P'. From the point of view of experimental work on the discharge between equipotential plates, the Hufford type of tube is unnecessarily complex.

(b) THE "BEAD."—Consideration of Hufford's results, and my own experiments with tubes such as those used by Hufford, indicate that there are two groups of phenomena at the hole in plate P.

(i.) There is "hetero-normal" or "hetero-abnormal" discharge from the wall and edge of the hole, resulting as it were in a foundation of negative glow in the hole ;

(ii.) A second glow, superimposed upon the first, with characteristics that are those of positive column striations in the same discharge tube.

In Hufford's tube glow (i.), particularly at high pressures, often exists independently of glow (ii.) (examples are given on page 1211*). The resistance of the kind described above for the U-cathode is overcome at the hole by the negative glow due to discharge from the wall of the hole, and discharge to the inner space between P, P' is the result. Glow (ii.) can be obtained at any similar constriction in the path of the Faraday Dark Space, or the negative glow. Thus, if P is disconnected from P', and only P' is used as cathode, the usual anode being retained, glow (ii.) is obtained at the hole in P. Thus the necessary overcoming of the resistance at the hole might conceivably be obtained as a result of the negative glow, or the glow (ii.). Glow (ii.) can exist in the hole without the discharge passing in the space PP'. Hence it is suggested that these experimental peculiarities, together with the results given by Hufford, concerning the pressures at which the bead appears and disappears in different gases, the dependence of the occurrence of the bead on the size of the hole, the current characteristics etc., point to the fact that some part of the phenomena at the hole has its explanation in the "hetero-normal" effect.

The superimposed glow gives three characteristics of the bead, namely, its round bead-like end (always turned away from the anode), its not infrequent striated nature, and much of its brightness ; its occurrence and shape through and in front of the hole are generally determined by the "hetero-normal" or "hetero-abnormal" glow on which it is presumed to lie.

An examination of Hufford's graph fig. 3, p. 1202,

* *Loc. cit.* Hufford.

showing results for the current passing to each of the plates P and P' confirms that the bead has a foundation of negative glow. No matter what the pressure, a definite current density is demanded for a given thickness of the C.D.S., and assuming that a minimum thickness of the C.D.S. must be obtained before it is possible for the bead condition to exist at the hole, it follows that a certain definite current density is similarly required. From Hufford's graph it is seen that the total current through the tube is approximately constant over the range of pressure 0.70 to 0.25 mm. Hg (for air), and that for the same range the current to plate P is nearly constant at 8.5 milliamperes.

The currents used by Hufford to give the bead effect are all strongly "abnormal." For purposes of comparison it would have been an advantage had "normal" currents been used. It is apparent that the maximum pressure at which the bead will occur depends upon whether or not the "normal" discharge condition is maintained at each value of the pressure, because the maximum thickness of the C.D.S. at any pressure is the "normal" one, and the foundation of the bead is a result of the "overlapping" of the C.D.S.'s. of opposing cathode surfaces. With small holes, the "hetero-normal" effect appears for "abnormal" values of the current to P. Hufford's table I.* gives the range of pressures over which the bead can be maintained for an aluminium cathode, and hole 2.6 mm. diameter. Now the pressures at which the C.D.S. is 1 cm. in length, when unit current is flowing ($i=10^{-4}$ ampere per sq. cm.) are:—0.70, 0.47, and 0.11 mm. Hg for helium, hydrogen, and air respectively: for these three gases therefore the "hetero-normal" effect would appear at a particular hole in the order: helium at the highest pressure, hydrogen at a lower pressure, and air at the lowest pressure. Assuming a minimum value of the pressure at which the bead can exist at the hole (of the nature of the minimum that is obtained for the U-cathode near the pressure 0.02 cm. Hg), the minimum pressure at which the bead should occur in the same three gases follows the same order, helium at the highest pressure, hydrogen at a lower, and air at the lowest pressure of the three. In general, for a particular hole, gases having the greater "normal" C.D.S. thickness pass as a bead at a higher pressure than gases having the smaller C.D.S. thickness. These considerations of the C.D.S. thickness applied to the condition for the "hetero-normal" effect

* *Loc. cit.* p. 1200.

to occur in a particular hole give the same results as were obtained experimentally by Hufford.

The bead should appear and disappear at a lower pressure for the hole of larger diameter. The value 0.42 on p. 1203 * is probably in error (see Table I. p. 1200), but the pressures given by Hufford at which the bead disappears (in the same table on p. 1203) follow the expected order. Again the values of the maximum pressures at which the bead effect occurs should be given for "normal" currents so that the results are strictly comparable.

The question of whether the "hetero-normal" and the "positive column glow" can exist together, or whether the "positive column glow" suppresses the "hetero-normal" one, cannot be completely answered from the above considerations, and an ultimate test will require the measurement of the current passing to the wall of the hole, apart from that passing to the surface of the plate P. A future paper, it is hoped, will deal with this question, together with the potential measurements reported by Hufford.

I am indebted to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled me to undertake the work.

XLIX. *The Milner and Debye Theories of Strong Electrolytes.* By GEORGE SCATCHARD †.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 178.)

IN a recent paper of this Journal, Pike & Nonhebel and Nonhebel & Hartley ‡ have published comparisons of the Milner and Debye theories, with conclusions very unfavourable to the latter. On account of the emphasis now being placed upon solutions of strong electrolytes, it seems desirable to show that the experiments of these authors do not necessarily lead to their conclusions.

Since both of these theories explain the deviations from the laws of ideal solutions, their exact forms depend upon

* *Loc. cit.* p. 1200.

† Communicated by the Author.

‡ Pike & Nonhebel, *Phil. Mag.* vol. 1. p. 723 (1925); Nonhebel & Hartley, *ibid.* p. 729.

the definition of the ideal solution. If this is defined as one in which the activity of each component is proportional to its mole fraction, the equation of Debye and Hückel becomes

$$-\log \gamma = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c + \log(1 + 0.002mw_1), \quad (1)$$

in which γ is the ratio of the activity, a , to the molality, m , in moles of electrolyte per kilogram solvent; c is the concentration in moles per litre; for a uni-univalent electrolyte at 25°, A is equal to $249.4/D^{\frac{3}{2}}$ (D = dielectric constant of solvent); in the same case α equals $2.06 \times 10^8 b/D^{\frac{1}{2}}$ (b = mean diameter of collision sphere of the ions, in centimetres); B is a complicated function of the temperature, ionic size, dielectric constant of the solvent and rate of change of the dielectric constant with changing electrolyte concentration.

Equation (1) contains two constants, α and B , which can be determined only approximately by independent measurements. Moreover, expansion of the first term on the right-hand side in a power series of c shows that the two are differentiated only in the coefficients of the three-halves and higher powers of c . So the equation may be simplified in dilute solutions. In the case of solvents of low dielectric constants, such as the alcohols, the term $B2c$ may be omitted, and the only effect will be to make the value of b calculated from α somewhat too large. In more dilute solutions the equation approaches

$$-\log f = A\sqrt{2c} - B'c, \quad . \quad . \quad . \quad . \quad (2)$$

in which $f = a/c$ and B' is a new constant. At zero concentration the equation approaches

$$-\log f = A\sqrt{2c}. \quad . \quad . \quad . \quad . \quad (3)$$

The formula of Milner cannot be expressed analytically. It gives the same values for all electrolytes of the same valence type, and values which do not differ very much from two-thirds those calculated from equation (3).

Nonhebel and Hartley compare the two theories with the experimental measurements of electromotive force of hydrochloric acid cells in water, ethyl alcohol, and methyl alcohol. They find that the Milner formula gives approximate agreement and that the Debye theory is much less satisfactory. In testing the Debye theory, however, they use equations (2) and (3) instead of equation (1). I have

discussed elsewhere* the comparison of the complete theory of Debye and Hückel with the experimental measurements in water, in ethyl alcohol, and in their mixtures, and found the agreement to be excellent. So the present discussion may be limited to the new measurements in methyl-alcohol solutions. Attention should be called, however, to the solubility measurements of Brönsted and La Mer†, which agree very closely with the Debye theory, but not at all with that of Milner.

Nonhebel and Hartley first test the two theories by the constancy of the quantity E_0 , which may be defined by the equation

$$E_0 = E + 0.1183 (\log c + \log f) = E - 0.0123 + 0.1183 (\log m + \log \gamma), \quad \dots \quad (4)$$

in which -0.0123 is equal to $0.1183 (\log c - \log m)$ for methyl alcohol at 25° , and E is the measured electromotive force. In their test of the Debye theory, $\log f$ is determined from equation (3). They later compare f , calculated by equation (2), with the values computed from the experimental measurements and the value of E_0 determined by the use of Milner's formula. Both tests are inconclusive, because Debye's theory is not represented by either of these equations through the concentration range of the experimental measurements; the second method also uses a quantity determined by the use of one theory in the test of another theory incompatible with the first.

The combination of equations (1) and (4), with insertion of the proper values for methyl alcohol ($D=30.2$), gives

$$E_0 = E - 0.0123 + 0.1183 [\log m - \log (1 + 0.064m)] - \frac{0.1767\sqrt{2c}}{1 + \alpha\sqrt{2c}} + B2c. \quad \dots \quad (5)$$

The values of c were computed by me from the approximate equation

$$c = \frac{m}{1.2716 + 0.02m}. \quad \dots \quad (6)$$

If B be given the value zero, which is justifiable in the concentration range studied, the experimental data are best fitted with $\alpha = 1.74$. Table I. and fig. 1 give the test of equation (5) and the comparison with the Milner formula.

* Journ. Am. Chem. Soc. xlvii. p. 2098 (1925).

† Brönsted & La Mer, Journ. Am. Chem. Soc. xlvi. p. 555 (1924).

In Table I. the first column gives the values of m ; the second the values of E_0 computed by Nonhebel and Hartley with Milner's formula; the third the deviations of the values of the second column from the value of E_0 accepted by these authors; the fourth column contains the values of E_0 computed from equation (5); and the fifth gives the deviations of the values of the fourth column from their average, -0.0226 volt. Fig. 1 shows the same results graphically. It differs from fig. 2 of Nonhebel and Hartley in that it extends to higher concentrations and in that the ordinates are shown on a ten times larger scale. No attempt is made to draw curves through the points. Instead, the two accepted values of E_0 are represented by horizontal dotted lines.

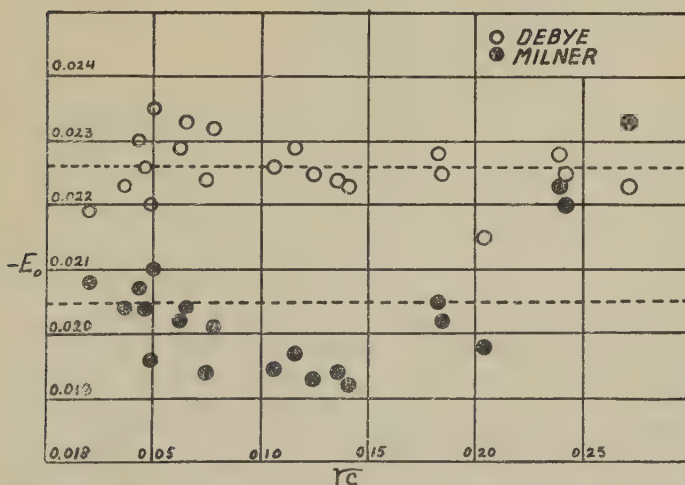
TABLE I.

Electromotive Force in Methyl Alcoholic Hydrochloric Acid at 25° .

m .	MILNER.		DEBYE.	
	$-E_0$.	$-E_0 - 0.0205$.	$-E_0$.	$-E_0 - 0.0226$.
0.0004955	0.0208	+0.0003	0.0219	-0.0007
0.001652	0.0204	-0.0001	0.0223	-0.0003
0.002363	0.0207	+0.0002	0.0230	+0.0004
0.002683	0.0204	-0.0001	0.0226	0.0000
0.002980	0.0196	-0.0009	0.0220	-0.0006
0.003161	0.0210	+0.0005	0.0235	+0.0009
0.004939	0.0202	-0.0003	0.0229	+0.0003
0.005425	0.0204	-0.0001	0.0233	+0.0007
0.007113	0.0194	-0.0011	0.0224	-0.0002
0.009857	0.0201	-0.0004	0.0232	+0.0006
0.01444	0.0194	-0.0011	0.0226	0.0000
0.01722	0.0197	-0.0008	0.0229	+0.0003
0.01986	0.0193	-0.0012	0.0225	-0.0001
0.02363	0.0194	-0.0011	0.0224	-0.0002
0.02549	0.0192	-0.0013	0.0223	-0.0003
0.04261	0.0205	0.0000	0.0228	+0.0002
0.04356	0.0202	-0.0003	0.0225	-0.0001
0.05312	0.0198	-0.0007	0.0215	-0.0011
0.07332	0.0223	+0.0018	0.0228	+0.0002
0.07333	0.0223	+0.0018	0.0228	+0.0002
0.07507	0.0220	+0.0015	0.0225	-0.0001
0.09467	0.0233	+0.0028	0.0223	-0.0003
0.1155	...	...	0.0229	+0.0003
0.4802	...	...	0.0234	+0.0008
0.5574	...	...	0.0224	-0.0002

It is obvious from either the table or the figure that the complete Debye equation gives an E_0 value more constant than the Milner formula. Not only is the average deviation smaller, even up to 0.04 M, but there is no trend in the deviations, and the equation holds equally well up to the highest concentrations measured, which are ten times those at which the Milner formula begins to deviate seriously. It is also apparent that E_0 calculated from the Debye equation is as constant as the consistency of the experimental data warrants, and -0.0226 volt may be taken as the most probable value for E_0 . It may be concluded that

Fig. 1.



these measurements, considering the enormous difficulties of precise measurement in very dilute alcoholic hydrochloric acid, offer very good confirmation of the Debye theory.

From the value of 1.74 for α , the mean diameter of the collision spheres is 4.65×10^{-8} cm. Other values for hydrogen chloride are: 4.05×10^{-8} in water, 4.06×10^{-8} in 50 mole per cent. ethyl alcohol, and 4.57×10^{-8} in ethyl alcohol*. Since the value in methyl alcohol is somewhat too large on account of the change in dielectric constant being neglected, the agreement is very satisfactory.

I have shown how the radius of the electrification sphere can be calculated from the E_0 values in different solvents with the assumption that all the deviation from ideality is due to the electrical work. To account for the behaviour

* Scatchard, *loc. cit.*

of hydrochloric acid in alcohol-water mixture, it was suggested that this size might change from 5 to 4×10^{-8} cm. between 50 and 95 mole per cent. alcohol. From these measurements in methyl alcohol and those of Danner in ethyl alcohol a value of 3.0×10^{-8} may be calculated. The calculation is not very accurate, because the difference in dielectric constants and between electrode potentials in terms of mole fractions are both very small. Since any change in size is to be attributed largely to the reaction $\text{H}_2\text{C}^+ = \text{H}^+ + \text{H}_2\text{O}$, the change between 95 and 100 mole per cent. might well be as great as that between 50 and 95 mole per cent. Considering the breadth of the assumptions and the large effect of a small experimental error the agreement is quite satisfactory.

The Milner Formula.

Although Milner and Debye start with the same fundamental theorems of electrostatics and statistical mechanics, the results they obtain do not agree quantitatively. Milner states that "It may be shown that, as an approximation, and when h^* is very small" the value of the virial of the ions is 1.253, or $\sqrt{\frac{\pi}{2}}$, that given by the limiting law of Debye, equation (3). Yet when h has the value corresponding to a concentration of 0.0001 M for a uni-univalent electrolyte in water at 0°, his virial is only 0.734 that of the equation (3), and the ratio decreases only to 0.656 in 0.2 M solution †. Most of this discrepancy may be attributed to inaccuracy in the Milner results. Milner himself continually refers to them as approximate. It seems probable that all his values are obtained by interpolation from the three values given in his first paper ‡. These results are obtained by graphic extrapolation from fifteen to infinity. To decrease substantially the range of extrapolation would require an amount of computation several thousand times that performed by Milner. It is worth while then to re-examine his method of extrapolation.

Since Milner's tables include data for only one of the three pairs of curves, his curves cannot be replotted accurately. Fig. 2, however, was obtained photostatically

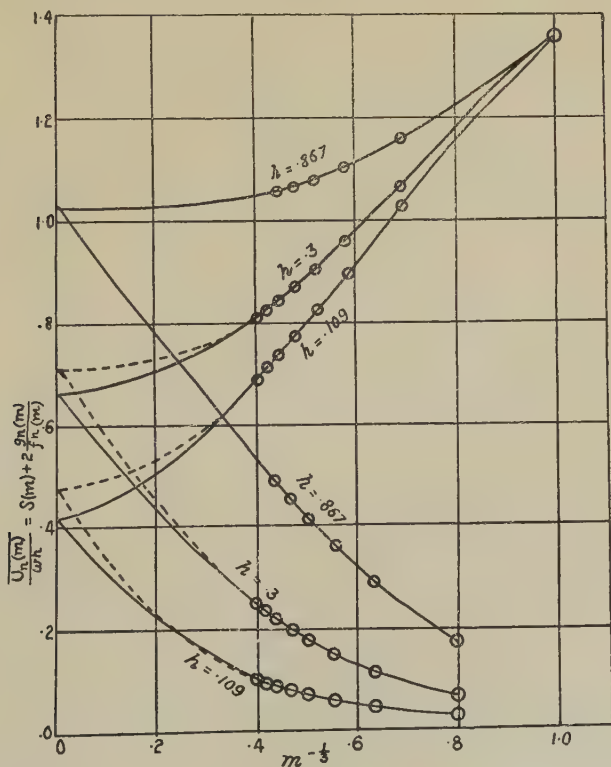
* h is a function of the ionic charge, the dielectric constant of the solvent, the temperature, and the concentration. By Milner's theory the virial is equal to $RT\bar{h}f(h)$.

† A. A. Noyes, Journ. Am. Chem. Soc. xlii. p. 1080 (1924).

‡ Milner, Phil. Mag. xxiii. p. 551 (1912).

without serious distortion. To quote Milner again, "The extrapolation of these curves to the axis is certainly a rather violent one, but it may be done with some confidence by observing the following points:—(1) The first curve must be everywhere below the limit and the second one everywhere above it; (2) the two curves must extrapolate to the same point on the axis; (3) from the fact that the virial of the ions external to the second arrangement is zero, it may

Fig. 2.



be inferred that the second curve for large values of m^* approaches the limit much more closely than the first one, and that it probably tends to become parallel to the axis as $m^{-1/2}$ becomes zero."

Inspection of fig. 2 shows that the dotted lines fulfil these conditions, especially the third, even better than do the full lines which represent Milner's extrapolation. The

* m is the number of ions whose effect on the virial is counted.

lowest pair might equally well be extrapolated to a still higher value. The results of the two extrapolations and the value of the Debye limiting law, equation (3), are given in Table II. The last two columns show the corresponding concentration of a uni-univalent electrolyte in water at 0° and in methyl alcohol at 25°. The most important conclusion to be drawn is that the Milner theory does not lead necessarily to the Milner formula, but may equally well give higher values for the slope. The values in the third column of Table II., which are shown in fig. 2 to be consistent with the Milner theory, were computed from the equation

$$f(h) = \frac{\sqrt{3}h}{1 + 0.35\sqrt{3}h}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

which at small concentrations must approach the Debye limiting law, which corresponds to $f(h) = \sqrt{3}h$.

TABLE II.

$f'(h)$ of Milner's Theory.

h .	$f(h)$. Milner.	$f(h)$. Eq. 4.	$f(h)$. Debye ($\sqrt{3}h$).	C_{H_2O} .	C_{MeOH} .
0	0	0	0	0.0	0.0
0.109	0.42	0.48	0.57	0.0007	0.00004
0.3	0.66	0.71	0.95	0.015	0.00085
0.867*	1.03	1.03	1.61	0.362	0.0206

There must, however, be a discrepancy between the results of Milner and the limiting law of Debye at finite concentrations, a discrepancy which increases with increasing concentration. There are two possible explanations: both methods give only approximations of the virial, the approximations may not be exactly the same; both methods consider the size of the ions in the early stages but ignore the size later, and the exact stage at which the size of the ions is ignored may influence the effect so that, relative to equation (3), the Milner theory may make a partial correction for ionic size. It would be an extremely tedious task to settle these points for the Milner theory. The Debye theory, on the other hand, is so direct in its development that the approximation may be improved at any time by including more terms in the series used to approximate the

* To quote Milner again: "This value of h is so large that the expression for the virial obtained in this paper would no longer be valid."

Boltzmann equation. It already gives a method for taking into account the size of the ions, and may readily be made more accurate in this respect whenever there is discovered a law for the repulsive forces between atoms more accurate than the rigid-sphere assumption.

The Determination of Free Energies from the Mutual Potential Energies of the Ions.

Pike and Nonhebel criticize the method of calculating the free energy from the mutual potential energy of the ions by an equation of the Gibbs-Helmholtz type, and claim that it cannot lead to quantitative results. Much of their argument is an attack on an equation of Debye and Hückel, given on page 725 between equations (10) and (11). This equation does not follow from the Debye theory without additional assumptions, and it is thermodynamically incompatible with the Debye theory for the free energy of the solutions. Although the equation is undoubtedly incorrect, that fact cannot effect the validity of the Debye theory.

Gross and Halpern* have given a justification of the method used by Milner and by Debye and Hückel, in which the relation between the mutual potential energy of the ions and the free energy of the solution is obtained by using the *partial* derivative of the free energy with respect to the temperature. They have also shown that the relation between the total internal energy of the solution and the free energy, for which the thermodynamics requires the *total* derivative with respect to the temperature, shows at least approximate agreement between the Debye theory and thermal measurements if the size of the ions varies slightly with the temperature.

Another confirmation of the exactness of this method is obtained from the fact that the same result has been obtained by three other methods, none of which depend on an integration with respect to the temperature. The first of these, used by Milner and by Nonhebel and Hartley, is to take the osmotic pressure as equal to the virial. The second, given by Noyes†, calculates the vapour-pressure of the ions from kinetic theory. These two are applicable only in dilute solutions. The third method‡ makes use of the difference in electrical work of charging the ions reversibly

* Gross & Halpern, *Physikalische Zeitschrift*, xxvi. p. 403 (1925).

† Noyes, *loc. cit.*

‡ Debye, *Physikalische Zeitschrift*, xxv. p. 97 (1924).

in the solution in question and in an infinitely dilute solution. It may be applied to solutions of any concentration.

Gross and Halpern* object to this last derivation on the grounds that the potential of any individual ion oscillates rapidly about the mean potential. This objection could be met by the invention of a device which would prevent the discharging of an ion and permit its charging only when its potential and charge each differ from the average by less than some infinitesimal amount. Such a device would increase the order of infinity of the time of the charging process, but that is unimportant in a purely theoretical process, in which the question of practical realizability is irrelevant.

The application of thermodynamic criteria to this step of the derivation is entirely beside the point, since one quantity involved—the mutual potential energy of the ions—cannot be represented by any of the ordinary thermodynamic equations; for these equations are incapable of dividing energy between the components of a phase. The final results may be tested thermodynamically by the application of the ordinary equations. In all tests so far made of the Debye theory, an agreement at least approximate has been found.

Cambridge, Massachusetts.

L. *The Milner and Debye Theories of Strong Electrolytes.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

OUR disagreement with Dr. Scatchard (*suprà*, p. 577) with regard to the activity coefficients of hydrogen chloride in methyl-alcohol solutions lies in the choice of the constant E_0 in the equation $E = E_0 - 0.1183 \log cf$. The value of E_0 can be obtained without any theoretical assumptions by plotting $E_0' = E + 0.1183 \log c$ against the square root of the concentration. The values of E_0' for hydrogen chloride in methyl alcohol are found to lie on a straight line within the limits of experimental error up to a concentration of 0.01 N, and they give a value for E_0 of -0.0205 volt. It was hoped that this quantity would be obtained more accurately by using the limiting equations of Milner and Debye in the manner described in our paper (*Phil. Mag.* (6) vol. l. p. 729, 1925). Dr. Scatchard has obtained the

* Gross & Halpern, *loc. cit.*

value $E_0 = -0.0226$ volt by making use of the complete Debye equation and adjusting the value of the mean diameter of the collision sphere of the ions until a constant value for E_0 was obtained. The figure on page 739 of our paper shows that this value is incompatible with the extrapolation of E_0' .

The constancy of E_0 values calculated from experimental results at higher concentrations, using the Debye equation, does not seem to us a sufficient reason for taking a value for E_0 which is inconsistent with the experimental results in less concentrated solutions.

We have been in correspondence with Professor Milner, and with his permission quote the following paragraph from his letter:—"Since I have read Debye's calculation critically, I think that his method of calculation of the effects of interionic force is greatly superior to mine. All the laborious summations and approximations contained in my calculation of 1912 are done away with, without any sacrifice of accuracy, by what seems to me a stroke of genius—namely, his observation that the average potential at a point of all the ions in a sphere containing a positive ion at the centre must satisfy Poisson's equation. Since the two calculations are based on the same assumptions and mine contains admitted approximations, I am inclined to believe that the numerical differences between them are to a large extent attributable to these. At any rate, I think this is the case

with regard to the $\sqrt{\frac{\pi}{2}}$ ratio, by which the limiting values of the internal energy at $h=0$ differ. In my footnote on this matter I said, 'It may be shown that, as an approximation, and when h is very small, $\bar{U} = -wh\sqrt{\frac{3\pi}{2}}h$.' The

statement was put in that form because it was clear to me that the coefficient was only an approximation even in the limit. The result was obtained, in fact, by a method which assumed that expressions for the average effect of all groups on the next ion outside them could be replaced by similar expressions for the effect of a group containing the average charge of the previously-mentioned groups. An assumption of this kind will only give an approximate result for the coefficient even in the limit when $h=0$, although the nature of the function would not be affected."

Yours faithfully,

Balliol College, Oxford.
April 28, 1926.

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LI. *On a Geometrical Presentment of the Constants of an Elastic Material.* By R. F. GWYHER, M.A.*

IN this paper I propose to construct the general expression for the potential function of strain per unit of volume in a material, on the assumption that the strain is small and that the material acts under strain as a conservative system. There is a further question, not here considered, as to whether the resulting stresses are such as can satisfy the mechanical stress equations.

The potential function will be a quadratic function of the six elements of strain, and it must possess permanency of form for any transformation of the coordinate axes, or must be an invariant quadratic function. It must also be positive for all small values of the elements of strain.

1. The general method which I employ here, as I have employed elsewhere, is an adaptation of the method of Differential Invariants and Covariants of Curves and Surfaces to apply to vectors, stresses, strains, etc., instead of purely geometrical subjects.

Imagine a small rotation of the coordinate axes about their own positions indicated by $\omega_1, \omega_2, \omega_3$ respectively, the material remaining stationary.

In consequence of this rotation, of which the components may be considered separately, there will be an alteration in the expressions considered which will depend upon their nature—as vectors, stresses, strains, and so forth. Generally, quantities showing similar characteristics will, on transformation of coordinate axes, alter in the same manner.

I shall employ $\Omega_1, \Omega_2, \Omega_3$ (which will be differential operators) to indicate the change consequent upon the rotations $\omega_1, \omega_2, \omega_3$ respectively, and their expressions will be found by forming the coefficients of $\omega_1, \omega_2, \omega_3$ respectively in the complete change. These operators will be distinctive in form for quantities of different kinds.

For example :

x will change to $x + \omega_3 y - \omega_2 z$, etc. ;

u will change to $u + \omega_3 v - \omega_2 w$, etc. ;

$\frac{\partial}{\partial x}$ will change to $\frac{\partial}{\partial x} + \omega_3 \frac{\partial}{\partial y} - \omega_2 \frac{\partial}{\partial z}$, etc. ;

$\frac{\partial u}{\partial x}$ will change to $\frac{\partial u}{\partial x} + \omega_3 \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) - \omega_2 \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)$, etc.

. . . (1)

* Communicated by the Author.

Hence, acting on a vector (u, v, w) or (x, y, z) ,

$$\begin{aligned}\Omega_1 &= w \frac{\partial}{\partial v} - v \frac{\partial}{\partial w}, & \Omega_2 &= u \frac{\partial}{\partial w} - w \frac{\partial}{\partial u}, & \Omega_3 &= v \frac{\partial}{\partial u} - u \frac{\partial}{\partial v}; \\ \Omega_1 &= z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z}, & \Omega_2 &= x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x}, & \Omega_3 &= y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y}.\end{aligned}\quad (2)$$

Taking the elements of strain from (1) and (2), we find

$$\Omega_1 = a \left(\frac{\partial}{\partial f} - \frac{\partial}{\partial g} \right) + 2(g-f) \frac{\partial}{\partial a} - c \frac{\partial}{\partial b} + b \frac{\partial}{\partial c}. \quad (3)$$

The expressions for Ω_2 and Ω_3 may be written down by a cyclic interchange.

As a further example, which I shall make use of later, write

$$\begin{aligned}X &= a^2 - 4fg, & Y &= b^2 - 4eg, & Z &= c^2 - 4ef, \\ \xi &= 4ae - 2bc, & \eta &= 4bf - 2ac, & \zeta &= 4cg - 2ab;\end{aligned}$$

by using (3), we shall find

$$\Omega_1 = \xi \left(\frac{\partial}{\partial Y} - \frac{\partial}{\partial Z} \right) + 2(Z-Y) \frac{\partial}{\partial \xi} - \zeta \frac{\partial}{\partial \eta} + \eta \frac{\partial}{\partial \zeta}, \quad (4)$$

which reproduces the form of (3).

If, again, we write

$$X = x^2, \quad Y = y^2, \quad Z = z^2, \quad \xi = 2yz, \quad \eta = 2zx, \quad \zeta = 2xy,$$

we again find

$$\Omega_1 = \xi \left(\frac{\partial}{\partial Y} - \frac{\partial}{\partial Z} \right) + 2(Z-Y) \frac{\partial}{\partial \xi} - \zeta \frac{\partial}{\partial \eta} + \eta \frac{\partial}{\partial \zeta}, \quad (5)$$

reproducing the form of (3) or (4).

2. If $Ax^2 + By^2 + Cz^2 + 2Dyz + 2Ezx + 2Fxy$, where x, y, z are the coordinates of a point in the material, is to be a covariantal expression retaining permanence of form for any transformation of coordinates, then $\Omega_1, \Omega_2, \Omega_3$ acting upon the terms in the expression must each produce a null result.

By making use of (5), we find that, acting on the coefficients only,

$$\Omega_1 = 2D \left(\frac{\partial}{\partial B} - \frac{\partial}{\partial C} \right) + (C-B) \frac{\partial}{\partial D} - F \frac{\partial}{\partial E} + E \frac{\partial}{\partial F}, \text{ etc.} \quad (6)$$

This is therefore the condition that

$$Ax^2 + By^2 + Cz^2 + 2Dyz + 2Ezx + 2Fxy = \text{constant} \quad (7)$$

should be the equation to a quadric traced in the material, and, retaining the same form in a change of coordinate system, may be called the equation to a covariant quadric.

On referring to (3), it will be seen that, under these conditions,

$$Ae + Bf + Cg + Da + Eb + Fc \quad . \quad . \quad . \quad (8)$$

is an invariant expression.

While from (4) it follows that

$$A(a^2 - 4fg) + B(b^2 - 4eg) + C(c^2 - 4ef) \\ + 2D(2ae - bc) + 2E(2bf - ac) + 2F(2cg - ab) \quad (9)$$

is also an invariant expression.

It is desirable to note that if $\{P, Q, R, S, T, U\}$ are the elements of stress, the expression for Ω_1 when acting on these elements is

$$\Omega_1 = 2S\left(\frac{\partial}{\partial Q} - \frac{\partial}{\partial R}\right) + (R - Q)\frac{\partial}{\partial S} - U\frac{\partial}{\partial T} + T\frac{\partial}{\partial U}, \quad (10)$$

and is of the same form as (6). Accordingly, the coefficients $\{A, B, C, D, E, F\}$ in a covariant quadric act on transformation of coordinate axes as the elements of stress act, in spite of the difference in dimensions.

3. We may now proceed to make use of (8) and (9) to construct the general invariantal expression of the second degree in the elements of strain, and for this purpose I shall, in the first instance, give a geometrical aspect to the question.

Imagine four concentric ellipsoids to be traced in the material under strain, arbitrary both as to the magnitude and orientation of their principal axes. Indicate their equations relative to their principal axes by

$$\alpha_0 x^2 + \beta_0 y^2 + \gamma_0 z^2 = M_0, \\ \alpha_1 x^2 + \beta_1 y^2 + \gamma_1 z^2 = M, \\ \alpha_2 x^2 + \beta_2 y^2 + \gamma_2 z^2 = M, \\ \alpha_3 x^2 + \beta_3 y^2 + \gamma_3 z^2 = M, \quad . \quad . \quad . \quad (11)$$

and their equations relative to arbitrarily chosen coordinate axes by

$$px^2 + qy^2 + rz^2 + 2syz + 2t zx + 2u xy = M, \quad . \quad (12)$$

with the proper subscript numbers in accordance with (11).

As the ellipsoids are fixed in the material, we may form invariantal expressions by using (8) and (9). From the first of the ellipsoids, I shall use (9) and obtain

$$p_0(a^2 - 4fg) + q_0(b^2 - 4eg) + r_0(c^2 - 4ef) \\ + 2s_0(2ae - bc) + 2t_0(2bf - ac) + 2u_0(2cg - ab), \quad (13)$$

which I shall indicate by A_0 .

This will form part of the invariant function of the second degree in strains which it is proposed to find.

As the ellipsoids are arbitrary, we shall be unable to increase the generality of the expression by adding a second invariant of the same character, for the sum would only amount to the substitution of one arbitrary invariant quantity for another.

From each of the other three ellipsoids we will form from (8) the invariant of the first degree,

$$p_1e + q_1f + r_1g + s_1a + t_1b + u_1c, \text{ etc.,}$$

which I shall indicate by B_1 , B_2 , and B_3 respectively. (14)

The general invariantal expression of the second degree is then

$$2V = A_0 + B_1^2 + B_2^2 + B_3^2. \quad . \quad . \quad . \quad (15)$$

It will be seen that the argument I have used against repeating such a term as A_0 does not apply to B_1^2 , etc.

This expression contains 24 coefficients or 24 apparent constants, but three of them are introduced by the arbitrary character of the coordinate axes.

As the first ellipsoid is, of necessity, specially treated in forming (15), we will suppose that the equations of the other ellipsoids are first transformed to the principal axes of the first ellipsoid and then to the arbitrary coordinate axes, in case that step is necessary.

But we shall have reduced the constants to 21, if we refer the equations of the four ellipsoids to the principal axes of the first. The coefficients will then contain the 12 coefficients in the equations of the four ellipsoids referred to their principal axes, and trigonometrical ratios of the three sets of three angles (conveniently the θ , ϕ , ψ employed in the Precession of the Equinoxes) which express the direction cosines of the principal axes of the last three of the ellipsoids referred to those of the first. This gives 12 dimensional constants, with the trigonometrical ratios of 9 angles, on which the 21 coefficients in the full expression for $2V$ depend.

4. The geometrical treatment which I have thought illuminating is not the only method which might be used.

If we take the equations of the four ellipsoids in the form given by (12) referred now to arbitrary coordinate axes, we may construct A_0 , B_1 , B_2 , B_3 as in (13) and (14), and finally $2V$ as in (15) as before, and then proceed as

follows:—By (9) and (10), the coefficients in A_0 , B_1 , etc., transform as the elements of stress transform, and may be expressed in terms of quantities corresponding to their principal or normal stress elements and the angles these normal elements make with the coordinate axes. We thus obtain an analysis similar to that obtained by the more geometrical method.

5. In the case of an isotropic material, we only need the first ellipsoid and one of the other three ellipsoids, and each of these two ellipsoids is to be a sphere, since the material is isotropic. Accordingly (15) becomes

$$2V = m(e + f + g)^2 + n(a^2 + b^2 + c^2 - 4fg - 4eg - 4ef) \quad (16)$$

in the usual form.

6. This paper does not deal with any physical aspect of the argument for reducing the number of elastic constants, but I think it throws light upon the discussion on the surfaces, based on the general expression for $2V$, found by Haughton in 1846, and discussed by Rankine and Saint Venant*.

Indicating the terms in $2V$ by reference to the strain elements forming the several terms, we may write

$$2V = \lambda_{11}e^2 + 2\lambda_{12}ef + 2\lambda_{13}eg + 2\lambda_{14}ea + 2\lambda_{15}eb \\ + 2\lambda_{16}ec + \text{etc.}, \quad (17)$$

where, in the subscript numbers, 1 denotes e , 2 denotes f , etc., and $P = \frac{\partial V}{\partial e}$ etc.

The “tasinomic” quartic is formed by writing x^2 for e , y^2 for f , etc., in the expression for $2V$, and the “orthotatic” ellipsoid is derived in the same way from the invariant $P + Q + R$.

These two surfaces are thus explained by the method of this paper. The other ellipsoid, named “heterotatic,” is explained in a different manner.

The equation given for this surface is

$$(\lambda_{44} - \lambda_{23})x^2 + (\lambda_{55} - \lambda_{13})y^2 + (\lambda_{66} - \lambda_{12})z^2 \\ + 2(\lambda_{14} - \lambda_{56})yz + 2(\lambda_{25} - \lambda_{46})zx + 2(\lambda_{36} - \lambda_{45})xy = 1. \quad (18)$$

* I cannot give the references. I think they are to be found in Todhunter's ‘History of Elasticity.’

The explanation is that, in accordance with (9),

$$\begin{aligned} &(\lambda_{44}-\lambda_{23})(a^2-4fg) + (\lambda_{55}-\lambda_{13})(b^2-4eg) \\ &+ (\lambda_{66}-\lambda_{12})(c^2-4ef) + 2(\lambda_{14}-\lambda_{56})(2ae-bc) \\ &+ 2(\lambda_{25}-\lambda_{46})(2bf-ac) + 2(\lambda_{35}-\lambda_{45})(2cg-ab) \end{aligned} \quad (19)$$

is an invariant expression, and is an essential part of $2V$. It is, in fact, that part of $2V$, as expressed in (17), which I have denoted by A_0 in (15), and which certainly appears in the simple case of isotropy in (16).

The reduction of the number of constants is not to be found by making the coefficients in (18) and (19) null.

Kirkland, Newbiggin,
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LII. *Intensity Variations in the Spectrum of Neon.* By
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[Plate X.]

Introduction.

COMPARATIVELY little experimental work has been done in connexion with the distribution of intensity in line spectra and the variations which can be produced under different conditions. The reason for this is probably to be found in the absence, until very recently, of any theoretical work which might serve as a basis for the interpretation of the results, and perhaps also in the absence of precision methods at all comparable in accuracy with those available for the measurement of wave-lengths. Of the various experimental devices for measuring the intensities of spectral lines, those which are based on the use of a thermopile and galvanometer are subject to the serious difficulties involved in maintaining a source of light constant in output over a considerable time. Photographic methods, on the other hand, while involving the peculiarities of the photographic plate, provide a simultaneous record of the whole of the lines in a spectrum under identical conditions of production.

One simple mode of procedure consists in the use of a neutral tinted wedge of absorbing material mounted in front of the slit of a spectrograph. This reduces the photographe

* Communicated by the Authors.

spectrum to a number of wedge-shaped lines of various lengths, and these lengths can be simply related to their "photographic" intensities. The theory of the neutral wedge has been largely developed by Merton and Nicholson *, and was applied by them to a study of the line spectrum of helium under various conditions.

Another method is described by Ornstein† which consists in passing the light through a series of parallel strips of absorbing material of different densities before focussing on the slit of the spectrograph. This would really be equivalent to an echelon-shaped "wedge" of absorbing material in front of the slit. What is then measured is not the length of the spectrum line, but (by means of a registering micro-photometer) the density of the various elements composing it. A graphical method is then used to determine the photographic intensity of one line compared with another. In both these methods it is necessary to determine the variation with wave-length of the absorbing power of the strips (or the wedge), in order to render possible the comparison of spectral lines differing appreciably in wave-length.

In connexion with multiple spectral lines Ornstein and his co-workers have been able to show that the intensity ratios of the components are a well-defined specific property of the emitting atom,—independent of exciting conditions,—and they have framed general rules for the formulation of these results. These rules are applicable also to the Zeeman-patterns of lines, and they have a straightforward interpretation on the basis of the Quantum Theory.

There is, as yet, however, no theoretical or empirical formulation of the energy distribution in a line series or spectrum. There are indeed many serious difficulties in the way of any attempt to formulate such a theory on the basis of experimental work. These difficulties arise from the numerous factors: type of discharge, current density, pressure of gas, presence of other gases, etc., which are all capable of modifying to some extent the "normal" intensity distribution. With this in view Hughes and Lowe‡ have investigated the line spectra of hydrogen and of helium as far as possible as a function of one variable, viz., the energy of impact of the exciting electrons. They found that a curve expressing the variation of intensity with the energy of the exciting electron

* Phil. Trans. A. vol. ccxvi. p. 459; vol. ccxvii. p. 237; vol. ccxx. p. 137.

† Proc. Phys. Soc. of London, vol. xxxvii. (5) p. 334 (1925).

‡ Phys. Rev. vol. xxi. p. 292 (1923); Proc. Roy. Soc. A. vol. civ. p. 480 (1923).

was characteristic in its general form of a particular series; but even under these simple conditions there is no simple law apparent which could be formulated mathematically. The whole question of the intensity distribution in a line spectrum is therefore very complex, and for the present it would scarcely seem possible to do more than collect and compare data in the cases of some simple gases.

The present investigation comprises a systematic record of the variations occurring in the spectrum of Neon. It was suggested originally by the exceptional variations of intensity of the line λ 5852, which had been observed visually during the course of some work on the effects of Neon on the spectra of other substances with which it was mixed. The very conspicuous variations of this line led us to consider the desirability of an extensive investigation of the Neon spectrum, in the hope that if such effects occurred in this case in an exaggerated form we might be able to correlate them to the series classification of Paschen*, and deduce some very general rules.

We have followed the experimental procedure of Merton and Nicholson and used a neutral tinted wedge throughout the work. We have also converted all our photographic intensities to absolute values by comparison with the radiation from the positive crater of the carbon arc (taken as black body radiation at an absolute temperature of 3750 degrees), following the method of these investigators in 1917. These absolute values have in each case been referred for convenience to that of λ 6402 as 100.0. Successive tables record the effects of current-density, condensed and "bulb" discharge, high and low pressure, admixture of hydrogen, argon, helium, and carbon dioxide, and the intensity distribution as a function of the distance from a flat cathode.

The whole of the results recorded in the present paper are for the visible spectrum only. It was originally intended to obtain a complete record for the ultra-violet also, by the use of a platinum wedge deposited on quartz as recommended recently by Merton†. A number of other things have so far prevented this, but it was felt desirable to record the fairly extensive work on the variations of the visible spectrum of Neon, deferring full discussion till they can be supplemented.

Reference to Paschen's papers shows that all the strong lines in the red, orange, and yellow (which constitute almost all the lines which could be photographed through the wedge

* *Ann. der Phys.* vol. lx. p. 405 (1919): vol. lxi. p. 201 (1920).

† *Proc. Roy. Soc. A.* vol. cvi. p. 378 (1924).

used) are the first members of different principal series. The second and higher members are mostly below $\lambda 3700$. With the ordinary discharge and normal exposures only two diffuse lines and one sharp line appeared, and these were comparatively faint. It is therefore clearly impossible with the present data to discuss the intensity distribution along a series, or satisfactorily to compare the principal and subordinate series together. This must be reserved till ultra-violet measurements are available. In the present paper discussion is therefore chiefly limited to a comparison of the various principal series among themselves (as typified by their first members). For this purpose we have grouped together the various principal series having a common final term: $1.5s_2$, $1.5s_3$, $1.5s_4$, $1.5s_5$, etc., and this arrangement has been adhered to throughout the various tables.

Experimental Detail.

The glass wedge employed was supplied by Messrs. Adam Hilger. The processes of calibration, *i. e.* the determination of the density gradient as a function of wave-length, were essentially the same as those described by Merton (*loc. cit.*). We have found that a tube filled with helium, when excited by an induction coil which was supplied with current from storage cells, is a reasonably constant source of light. For the process of reducing the light in a known ratio we have used copper foil perforated with circular holes by a punch. The optical density of these could be relied on to a high degree of accuracy. We found it convenient to use two such plates in the calibration of the neutral wedge (optical densities 0.4845 and 0.8216) for the weaker and stronger lines respectively. The "photographic" intensity of a line is related to the optical density of the wedge (d_λ), its height (h) on the plate, and the magnification (m) of the spectrograph by the formula:

$$I_{(\text{Photo.})} = \log_{10}^{-1} \frac{d_\lambda h}{m}.$$

This expression, of course, does not take into account the varying sensitivity of the photographic plate with wave-length. The conversion of photographic intensities to absolute values was done by multiplying by the factor

$$\left[\frac{\text{Absolute Intensity of Carbon arc}}{\text{Photographic Intensity of Carbon arc}} \right]_\lambda,$$

where the positive crater of the carbon arc was recorded on

the same plate, and its photographic intensities were deduced from measurements of "*h*" for various wave-lengths. As already mentioned, the absolute radiation for a given wave-length was calculated from the formula of Wien :—

$$I_{\text{Abs.}} = \lambda^{-5} e^{-\frac{1.445}{3750\lambda}},$$

taking the value for $\lambda = 3888 \cdot 10^{-8}$ cm. arbitrarily as unity (as suggested by Merton). The values were, of course, corrected for the dispersion of the spectrograph.

We found it possible to measure the heights of lines directly from the negatives taken. We used Ilford Rapid Process plates throughout, and "cut" these slightly with potassium ferricyanide so as to give a very sharp end point.

The effect of irradiation, which is large for the strong lines, was eliminated by arranging that the cross-wire of the measuring micrometer ran from the base of one very weak line to the base of another, in both of which the effect was apparently negligible. Allowing for these things any error in "*h*" is probably less than one per cent. for most lines. Assuming the process of "cutting" a subtractive one, as seems reasonable, the degree of cutting is immaterial so long as the wedge spectrum in question and the spectrum of which the absolute intensities are known are taken on the same plate, and therefore have the same subsequent treatment.

For

$$\frac{10^{-\frac{d_{\lambda}(h_1-x)}{m}}}{10^{-\frac{d_{\lambda}(h_2-x)}{m}}} = \frac{10^{-\frac{d_{\lambda}h_1}{m}}}{10^{-\frac{d_{\lambda}h_2}{m}}},$$

where x = amount cut off each line.

It is not, however, permissible to use the photographic intensities of the carbon arc from one plate in order to deduce the absolute intensities of the lines on another, even if taken from the same batch. For if h_1 = original height of a line of wave-length λ and h_2 = the corresponding height in the carbon arc, while x is the height cut off from the first and y from the second :

$$\frac{10^{-\frac{d_{\lambda}(h_1-x)}{m}}}{10^{-\frac{d_{\lambda}(h_2-y)}{m}}} = 10^{\frac{d_{\lambda}(x-y)}{m}} \times \frac{10^{-\frac{d_{\lambda}h_1}{m}}}{10^{-\frac{d_{\lambda}h_2}{m}}},$$

so that the absolute value of the line in question is in error by the factor $10^{\frac{d_{\lambda}(x-y)}{m}}$. As all the lines are referred to

some particular one, as 100 say, this error would be eliminated, but for the factor varying with d_λ through the spectrum, *e. g.* with the particular wedge used and assuming $x-y=\frac{1}{4}$ mm. say, the factor is 1.268 at λ 6717 and 1.481 at λ 4340.

The absolute values of the Neon lines in Table I. were deduced from a good plate on which the positive crater of the carbon arc was photographed in addition to the Neon

TABLE I.

Photographic and Absolute Intensities of Neon Lines.
(Uncondensed Discharge.)

Wave-length.	Abs. Int. of C. arc.	Photo. Int. of C. arc.	Abs./Photo. of C. arc.	Neon. Photo. Int.	Neon. Abs. Int.	Series.
7245	55.90	6.552*	8.53	0.55	84.3	$1.5s_1-2p_{10}$
7174	54.09	11.09*	4.88	0.42	37.0	$1.5s_2-2p_4$
7032	50.40	31.63*	1.59	4.45	127.2	$1.5s_3-2p_{10}$
6929	47.75	66.73	0.715	6.29	80.9	$1.5s_2-2p_6$
6717	42.31	210.8	0.201	12.55	45.4	$1.5s_2-2p_5$
6678	41.33	254.1	0.163	20.14	59.1	$1.5s_2-2p_4$
6599	39.38	357.6	0.110	17.70	35.0	$1.5s_2-2p_2$
6533	37.74	449.2	0.0840	18.09	27.3	$1.5s_3-2p_7$
6506	37.07	489.7	0.0757	45.06	61.4	$1.5s_4-2p_8$
6402	34.62	622.4	0.0556	100.0	100.0	$1.5s_3-2p_9$
6383	34.19	631.4	0.0542	48.37	47.2	$1.5s_1-2p_7$
6334	33.02	663.6	0.0498	46.24	41.4	$1.5s_2-2p_8$
6305	32.34	682.2	0.0474	20.06	17.1	$1.5s_1-2p_6$
6266	31.45	716.4	0.0439	28.62	22.6	$1.5s_3-2p_5$
6217	30.34	651.0	0.0466	17.35	14.5	$1.5s_3-2p_7$
6182	29.38	680.1	0.0432	1.020	0.79	$2p_9-3.5s_5$
6164	29.16	694.9	0.0420	19.34	14.6	$1.5s_3-2p_2$
6143	28.69	714.2	0.0402	47.69	34.5	$1.5s_5-2p_6$
6096	27.68	722.8	0.0383	34.99	24.1	$1.5s_1-2p_4$
6074	27.20	687.9	0.0395	27.23	19.4	$1.5s_1-2p_3$
6030	26.16	645.5	0.0405	9.82	7.16	$1.5s_4-2p_2$
5992	25.22	585.7	0.0431	0.58	0.45	$2p_6-4d_3$
5988	25.22	585.7	0.0431	0.58	0.45	$2p_6-4d_3$
5975	25.10	557.5	0.0450	8.06	6.52	$1.5s_5-2p_5$
5945	24.47	533.3	0.0459	23.31	19.2	$1.5s_5-2p_4$
5902	23.61	474.2	0.0411	1.44	1.07	$2p_4-3.5s_1$
5882	23.17	444.8	0.0521	13.29	12.5	$1.5s_5-2p_2$
5852	22.62	415.5	0.0544	41.75	40.9	$1.5s_2-2p_1$
5820	21.98	375.8	0.0585	1.06	1.12	$2p_4-4d_4$
5804	21.66	358.5	0.0604	0.44	0.48	$2p_4-4d_1$
5764	20.88	317.4	0.0658	1.49	1.76	$2p_3-4d_1$
5748	20.56	300.9	0.0683	0.41	0.51	$2p_3-4d_1$
5401	14.46	148.4	0.0974	0.94	1.65	$1.5s_4-2p_1$
5343	13.54	128.3	0.106	0.56	1.06	$2p_{10}-4d_6$
5341	13.54	128.3	0.106	0.56	1.06	$2p_{10}-4d_7$
5331	13.36	124.7	0.107	0.50	0.96	$2p_{10}-4d_3$

* Becoming inaccurate owing to the insensitivity of the plate.

wedge-spectrum. By "ordinary" Neon spectrum is meant the light from a Plücker type of capillary tube of about 1 mm. bore, filled with gas to a pressure corresponding to 1 mm. dark space.

Table II. shows the effect of different types of discharge on the "ordinary" Neon spectrum. By "bulb" discharge is meant the light from the wide bulb part of the tube when a very mild condensed discharge was passed.

TABLE II.

Comparison of Absolute Intensities in Ordinary, Bulb,
and Condensed Discharges.

Series.	<i>n</i> .	Wave-length.	P.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .	<i>c/b</i> .
1·5s ₅ —2 <i>p_n</i>	9	6402	20	100	100	100	1·00	1·00	1·00
	8	6334	10	41·4	58·8	60·9	1·42	1·47	1·04
	7	6217	15	14·5	28·6	32·8	1·97	2·26	1·15
	6	6143	12	34·5	52·9	64·5	1·53	1·87	1·22
	5	5975	12	6·52	19·6	20·4	3·01	3·13	1·04
	4	5945	10	19·2	42·8	44·7	2·23	2·33	1·04
	2	5881	20	12·5	28·5	39·0	2·28	3·12	1·37
1·5s ₄ —2 <i>p_n</i>	8	6506	15	61·4	82·3	87·2	1·34	1·42	1·06
	7	6383	12	47·2	65·6	80·2	1·39	1·70	1·22
	6	6305	6	17·1	35·6	39·0	2·08	2·28	1·09
	4	6096	8	24·1	45·3	55·9	1·88	2·32	1·23
	3	6074	10	19·4	32·4	45·6	1·67	2·35	1·41
	2	6030	10	7·16	17·5	23·8	2·44	3·32	1·36
1·5s ₃ —2 <i>p_n</i>	10	7032	10	127	201	146	1·58	1·15	0·726
	7	6533	6	27·3	48·9	55·7	1·79	2·04	1·14
	5	6266	15	22·6	38·6	50·9	1·71	2·25	1·32
	2	6164	12	14·6	28·3	42·6	1·94	2·92	1·50
1·5s ₂ —2 <i>p_n</i>	6	6929	10	80·9	124	127	1·53	1·57	1·02
	5	6717	2?	45·4	73·5	84·9	1·62	1·87	1·15
	4	6678	9	59·1	86·9	101	1·47	1·71	1·16
	2	6599	15	35·0	57·1	76·3	1·63	2·18	1·34
	1	5852	50	40·9	64·2	65·8	1·57	1·61	1·02
2 <i>p₄</i> —3·5s ₁	—	5902	6	1·07	4·62	3·79	4·32	3·54	0·820
2 <i>p₃</i> —4 <i>d</i>	—	5820	10	1·12	5·00	3·81	4·46	3·40	0·762
2 <i>p₂</i> —4 <i>d₁</i>	—	5764	15	1·76	7·76	5·93	4·41	3·37	0·764

P=Intensity according to Paschen.
a=Intensity of ordinary discharge.
b=Intensity of bulb discharge.
c=Intensity of condensed discharge.

It will be noted that the various principal series of any one group diminish in intensity with diminishing wave-length.

The bulb discharge enhances all the principal series, the degree of enhancement in any one group increasing with diminishing wave-length. The same effect is apparent with the condensed discharge, *e.g.* the s_4 and s_3 groups show it without exception. The effect c/b is, however, much less than b/a .

These facts account for the intense yellow colour of the light from Neon tubes excited by the condensed discharge, in contrast with the deep orange colour under normal excitation.

A few lines show anomalous variations, usually in both the condensed and bulb discharges (if at all). $\lambda 5975$, which is very weak ordinarily, shows exceptional enhancement under these conditions. The intensity of $\lambda 6143$ appears to vary in such a way as to compensate that of its neighbour $\lambda 5975$. The line $\lambda 6305$ is unduly weak in the condensed discharge, while $\lambda 5852$, a yellow line which shows many notable variations—as will be seen later—is enhanced to the average extent by a bulb discharge, but left unchanged by a condensed discharge. There are two diffuse lines and one sharp line (a quartet) recorded under all the conditions of excitation. The effect of a bulb discharge on these is a very strong enhancement,—over fourfold,—and of a different order to that of the principal lines. In further contrast to the latter the condensed discharge then reduces the degree of enhancement. The two diffuse series show almost identical behaviour in this respect, though—as in the case of helium—the effect may only be a reduction of the central intensities, and not of the energy content of the lines, which are probably broadened. The effects of the bulb and condensed discharges would therefore be sufficiently different to distinguish the subsidiary series from the principal series of a spectrum.

Table III. shows the influence of high pressure (25 mm.) on the development. Referred to the usual standard of 100 for $\lambda 6402$, most of the lines are enhanced (*vide b/a* column), although a few in the yellow are reduced. The regularity is somewhat broken, but there is a tendency for the less refrangible series of a group to exhibit the greater enhancement (*vide* the $1.5s_3-2p_n$ group). This accounts for the deeper orange colour of the high pressure tubes.

Correlating the c/b column of Table III. with the c/a column of Table II., we have a comparison of the behaviour of the condensed discharge under different conditions of pressure. It is true that the intensity of the condensed discharge cannot be reproduced in successive experiments, and that therefore the broadening of the lines may be different

and the central intensities alter as a consequence. Indeed, with the 25 mm. tube the condensed discharge was probably milder, and therefore for the same energy content of a line the central intensity should be more pronounced. It will be seen, however, from the respective columns of Tables II. and III., that without exception the enhancement due to the condensed discharge is less at high pressure than at low pressure for the s_5 , s_4 , and s_3 groups. In the s_2 group the intensities are comparable and show an enhancement in some cases. Possibly this is accounted for by the above facts.

TABLE III.

Influence of Pressure (Absolute Intensities).

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .	<i>c/b</i> .
$1\cdot5s_5-2p_n$	9	6402	100	100	100	1.000	1.000	1.000
	8	6334	41.4	42.6	50.2	1.029	1.212	1.178
	7	6217	14.5	16.7	25.1	1.152	1.731	1.503
	6	6143	34.5	44.8	52.8	1.229	1.529	1.177
	5	5975	6.52	5.89	17.1	0.903	2.623	2.903
	4	5945	19.2	19.2	35.3	1.000	1.836	1.836
	2	5882	12.5	12.5	30.8	1.000	2.464	2.464
$1\cdot5s_4-2p_n$	8	6506	61.4	67.9	85.0	1.106	1.384	1.252
	7	6383	47.2	67.3	71.3	1.426	1.511	1.059
	6	6305	17.1	15.8	26.8	0.924	1.567	1.696
	4	6096	24.1	28.3	41.5	1.174	1.722	1.466
	3	6074	19.4	18.3	34.1	0.943	1.758	1.863
	2	6030	7.16	7.23	18.5	1.010	2.584	2.559
$1\cdot5s_3-2p_n$	10	7032	127	270	241	2.126	1.898	0.893
	7	6533	27.3	36.3	53.5	1.330	1.960	1.474
	5	6266	22.6	29.4	40.9	1.301	1.810	1.391
	2	6163	14.6	16.3	23.3	1.116	1.596	1.429
$1\cdot5s_2-2p_n$	6	6929	80.9	93.4	177	1.154	2.188	1.895
	5	6717	45.4	58.6	114	1.291	2.511	1.945
	4	6678	59.1	75.7	134	1.281	2.267	1.770
	2	6599	35.0	44.8	93.2	1.280	2.663	2.080
	1	5852	40.9	19.3	55.1	0.472	1.347	2.855
$2p_4-3\cdot5s_1$	—	5902	1.07	—	—	—	—	—
$2p_3-4d_4$	—	5820	1.12	—	—	—	—	—
$2p_2-4d_4$	—	5764	1.76	—	—	—	—	—

a = Capillary tube—Ordinary uncondensed discharge.*b* = Capillary tube—Uncondensed discharge—25 mm. pressure.*c* = Capillary tube—Mild condensed discharge—25 mm. pressure.

As before, λ 5975 is a line of exceptional variation, being reduced in intensity at high pressure, but showing exceptional enhancement in the condensed discharge. The compensating

behaviour of $\lambda 6143$ is again apparent. $\lambda\lambda 6305, 6074$ show a slight reduction in high pressure, which, however, is obscured by the condensed discharge. $\lambda 5852$ again shows large variations, being reduced to 0.472 of its value by high pressure. The condensed discharge, although enhancing it by the large factor 2.85, leaves it still of exceptionally low intensity as compared with its neighbours in the group. It will be seen later that $\lambda 5852$ is essentially a "low pressure" line. As at "ordinary" pressure, so at high pressure the condensed discharge displaces the energy towards the more refrangible principal series of a group.

The lines $\lambda 5902$ (sharp), and $\lambda\lambda 5820$ and 5764 (diffuse) do not appear at high pressure, *even on some comparatively strong plates* (either with uncondensed or condensed discharges). Though it would be unwise to generalize on so small a basis, it is possible, therefore, that high pressure tends to throw the energy into the principal series at the expense of the subsidiary series.

From the *b/a* column of Table IV. it is clear that the effect of low current density (such as would obtain in a tube of 15 mm. bore compared with a capillary bore of 1 mm.) is to displace the energy to the less refrangible principal series of any group. With slight irregularities this is noticeable in the s_5, s_4 , and s_3 groups, and it is the reason for the pronounced red colour of pure Neon in wide bore discharge tubes. The effect apparently reverses in the s_2 group, the reversal being similar to that previously recorded in connexion with Table III., in which the displacement of energy to the more refrangible side by the condensed discharge was compared at different pressures.

The general effect of very low pressure (*vide* column *c/b*) is to displace the energy towards the more refrangible series in any group: the opposite effect of very high pressure.

The lines $\lambda\lambda 6143, 5975$, as before, show anomalous variations under low current density, the former being reduced by comparatively little, and the latter by too much, while low pressure has no notable effect. $\lambda 5852$ is tremendously reduced in intensity by low current density, and equally notably enhanced at very low pressure. Under the latter condition it becomes the dominating line in the spectrum, much as the green line $\lambda 5015$ of helium behaves under similar circumstances. It is perhaps noteworthy that $\lambda 5015$ is a member of the principal series of singlets of helium.

The two diffuse lines $\lambda\lambda 5820, 5764$, of which we saw no sign under conditions of high pressure (*vide* Table IV.), are

notably enhanced at very low pressure—viz., by the factors 6·88, 5·35. The sharp line λ 5902 does not appear.

The low pressure photograph gave the following three lines of helium and two of hydrogen with the approximate intensities indicated:— $\lambda\lambda$ 5015, (51); 4713, (15); 4471, (13); 6563, (65); 4861, (11). These gases could only have been present, however, in *very* small proportions.

TABLE IV.
Effect of Very Low Pressure and Current Density.

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>) *.	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .	<i>c/b</i> .
$1\cdot5s_5-2p_n$	9	6402	100	100	100	1·000	1·000	1·000
	8	6334	41·4	24·9	52·4	0·601	1·266	2·104
	7	6217	14·5	5·13	14·0	0·354	0·966	2·729
	6	6143	34·5	23·9	51·6	0·693	1·496	2·159
	5	5975	6·52	—	9·46	—	1·451	—
	4	5945	19·2	6·66	27·9	0·347	1·453	4·189
	2	5882	12·5	4·96	26·2	0·397	2·096	5·282
$1\cdot5s_4-2p_n$	8	6506	61·4	75·4	121	1·228	1·971	1·605
	7	6383	47·2	44·8	62·6	0·949	1·345	1·397
	6	6305	17·1	6·35	17·2	0·371	1·006	2·709
	4	6096	24·1	9·99	43·1	0·415	1·788	4·314
	3	6074	19·4	6·73	32·2	0·347	1·660	4·785
	2	6030	7·16	2·60	10·2	0·363	1·425	3·923
$1\cdot5s_3-2p_n$	10	7032	127	235	—	1·850	—	—
	7	6533	27·3	22·1	29·3	0·810	1·073	1·326
	5	6266	22·6	10·9	28·3	0·482	1·252	2·596
	2	6163	14·6	5·31	19·4	0·364	1·329	3·653
$1\cdot5s_2-2p_n$	6	6929	80·9	56·3	156	0·696	1·928	2·771
	5	6717	45·4	28·1	82·6	0·619	1·819	2·940
	4	6678	59·1	40·6	136	0·687	2·301	3·350
	2	6599	35·0	24·8	63·4	0·709	1·811	2·556
	1	5852	40·9	4·41	173	0·108	4·230	39·23
$2p_4-3\cdot5s_1$	—	5902	1·07	—	—	—	—	—
$2p_3-4d_1$	—	5820	1·12	—	6·86	—	6·13	—
$2p_3-4d_4$	—	5764	1·76	—	8·25	—	4·69	—

a = Capillary tube—Ordinary discharge—about 1 mm. pressure.

b = Wide bore tube—25 mm. pressure.

c = Wide bore tube—Very low pressure.

* This tube unfortunately contained a trace of carbon, which may have superposed a specific effect on that due to high pressure Neon in a wide bore tube.

TABLE V.

Effect of Admixture of Hydrogen.

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .	<i>c/b</i> .
$1\cdot5s_5-2p_n$	9	6402	100	100	100	1.000	1.000	1.000
	8	6334	41.4	43.3	26.2	1.046	0.634	0.606
	7	6217	14.5	13.6	5.21	0.938	0.359	0.383
	6	6143	34.5	35.0	40.8	1.014	1.181	1.165
	5	5975	6.52	6.26	4.45	0.960	0.683	0.711
	4	5945	19.2	19.5	17.2	1.016	0.897	0.883
	2	5882	12.5	11.4	10.7	0.912	0.855	0.938
$1\cdot5s_4-2p_n$	10	7245	84.3	57.9	—	0.687	—	—
	8	6506	61.4	59.2	61.5	0.966	1.001	1.037
	7	6383	47.2	49.8	35.5	1.055	0.752	0.712
	6	6305	17.1	17.9	9.13	1.047	0.534	0.510
	4	6096	24.1	23.2	25.4	0.963	1.052	1.093
	3	6074	19.4	19.5	17.0	1.007	0.877	0.871
	2	6030	7.16	7.06	5.12	0.986	0.715	0.725
	1	5400	1.65	0.72	—	0.436	—	—
$1\cdot5s_3-2p_n$	10	7032	127	93.8	—	0.737	—	—
	7	6533	27.3	26.7	23.4	0.987	0.858	0.878
	5	6266	22.6	24.3	18.6	1.075	0.823	0.766
	2	6163	14.6	16.0	11.0	1.096	0.755	0.689
$1\cdot5s_2-2p_n$	6	6920	80.9	60.5	66.8	0.748	0.825	1.104
	5	6717	45.4	36.5	32.6	0.804	0.719	0.894
	4	6678	59.1	49.5	57.0	0.838	0.965	1.152
	2	6599	35.0	29.5	31.9	0.843	0.911	1.081
	1	5852	40.9	38.3	126	0.936	3.076	3.285
$2p_9-3\cdot5s_5$	—	6182	0.79	0.68	—	0.861	—	—
$2p_4-3\cdot5s_1$	—	5902	1.07	1.21	—	1.131	—	—
$2p_6-4d_4$	—	5991	0.45	0.42	—	0.933	—	—
$2p_6-4d_3$	—	5988						
$2p_8-4d_4$	—	5820	1.12	1.09	—	0.973	—	—
$2p_9-4d_4$	—	5764	1.76	1.62	—	0.920	—	—
$2p_{10}-4d_6$	—	5343	1.06	0.88	—	0.830	—	—
$2p_{10}-4d_5$	—	5341						
$2p_{10}-4d_3$	—	5330	0.96	0.73	—	0.760	—	—
H_α	—	6562	—	1.37	691	—	—	504
H_β	—	4861	—	—	236	—	—	—
H_γ	—	4340	—	—	65.6	—	—	—
H_δ	—	4102	—	—	7.53	—	—	—

a = Pure Neon.*b* = Neon with a trace of hydrogen.*c* = Neon with a quantity of hydrogen.

The data of Table V. were obtained by admitting hydrogen through a palladium regulator into the Plücker tube containing "ordinary" low pressure Neon. The admixture of a trace of hydrogen produces comparatively little alteration.

It is probably true to say that within the limits of experimental error the effect is negligible on the s_5 and s_4 groups, with a tendency to displace the energy to the more refrangible series in the s_3 and s_2 groups. A quantity of hydrogen affects a general reduction of intensity, but there is no apparent regularity. The c/b and c/a columns show that the reduction is different for the different lines. The greater part of the light emission in case (c) arises from the Balmer Series: the photographic intensities of the recorded Neon lines were all comparatively small. The behaviour of $\lambda 5852$ is again notable. A quantity of hydrogen affects a three-fold enhancement of this line, in striking contrast to the other lines of Neon.

Column (b) of Table VI. exhibits some noteworthy changes. The very considerable intensity reduction of all the lines is at once apparent. This accords naturally with the fact that they disappear completely for greater proportions of argon. The reduction, however, is not uniform, but exhibits a pronounced intensity displacement towards the red end in each group. This of course may be due either to the high pressure together with the low current density consequent upon using a wide bore tube, or to the specific action of argon, or to both of these causes. A comparison with the b/a column of Table IV. (which is reproduced in Table VI.) shows that with the possible exception of the s_2 group the former cause accounts for the whole of this. Column c/a shows, with some fluctuations, an energy displacement towards the shorter wave-lengths. There are, however, five factors concerned in this intensity distribution: mild condensed discharge conditions, low current density, high pressure of gas, the presence of a little hydrogen, and the presence of a trace of argon. We proceed to attach weight to these in comparison with results already obtained.

Comparison with the b/a and c/a columns of Table II. shows a satisfactory correspondence throughout the s_5 and s_4 groups, the intensities in question being intermediate between these values. In the s_3 and s_2 groups the discharge conditions cannot account wholly for the intensities, which are in general greater than those of Table II. Consider now the c/a column of Table III., which includes the same conditions of discharge and pressure. Compared with these the intensities of Table VI. (column c/a) are uniformly greater and show, particularly in the s_3 and s_2 groups, evidence of an additional energy displacement to the shorter wave-lengths. The effect of low current density (*vide* the b'/a column) is the reverse of this. There remain the effects of hydrogen and argon

TABLE VI.

Trace of Argon in 25 mm. Neon (wide bore).

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b</i> / <i>a</i> .	<i>b</i> / <i>a</i> .	<i>c</i> / <i>a</i> .
$1.5s_n-2p_n$	9	6402	100	100	100	1.000	1.000	1.000
	8	6334	41.4	20.0	56.4	0.601	0.483	1.362
	7	6217	14.5	—	29.1	0.354	—	2.008
	6	6143	34.5	17.2	59.4	0.693	0.497	1.722
	5	5975	6.52	—	20.3	—	—	3.117
	4	5945	19.2	5.32	45.1	0.347	0.277	2.349
	2	5882	12.5	—	32.6	0.397	—	2.608
$1.5s_4-2p_n$	10	7245	84.3	—	185	—	—	2.190
	8	6506	61.4	38.8	84.8	1.228	0.632	1.381
	7	6383	47.2	34.5	77.6	0.949	0.731	1.645
	6	6305	17.1	—	30.9	0.371	—	1.806
	5	6128	—	—	9.70	—	—	—
	4	6096	24.1	8.60	47.2	0.415	0.357	1.957
	3	6074	19.4	5.82	38.2	0.347	0.300	1.971
	2	6030	7.16	—	21.4	0.363	—	2.983
	1	5400	1.65	—	5.43	—	—	3.291
$1.5s_3-2p_n$	10	7032	127	—	254	1.850	—	1.998
	7	6533	27.3	18.9	66.9	0.810	0.693	2.449
	5	6266	22.6	9.63	50.9	0.482	0.426	2.253
	2	6163	14.6	4.12	36.7	0.364	0.282	2.514
$1.5s_2-2p_n$	6	6929	80.9	—	162	0.696	—	2.000
	5	6717	45.4	—	115	0.619	—	2.524
	4	6678	59.1	49.0	138	0.687	0.829	2.333
	2	6599	35.0	22.1	88.6	0.709	0.630	2.530
	1	5852	40.9	—	94.2	0.108	—	2.304
$2p_9-3.5s_5$	—	6182	0.79	—	2.25	—	—	2.848
$2p_4-3.5s_1$	—	5902	1.07	—	5.14	—	—	4.804
$2p_8-4d_4$	—	5991	0.45	—	2.41	—	—	5.356
$2p_6-4d_3$	—	5988		—		—	—	
$2p_3-4d_4$	—	5820	1.12	—	5.01	—	—	4.473
$2p_8-4d_1$	—	5804	0.48	—	1.97	—	—	4.104
$2p_9-4d_4$	—	5764	1.76	—	8.39	—	—	4.767
$2p_9-4d_1$	—	5748	0.51	—	2.33	—	—	4.569
$2p_9-5d_4$	—	5037	—	—	3.16	—	—	—
$2p_{10}-4d_6$	—	5343	1.06	—	5.98	—	—	5.642
$2p_{10}-4d_5$	—	5341		—		—	—	
$2p_{10}-4d_3$	—	5331	0.96	—	5.36	—	—	5.583
$2p_{10}-5d_6$	—	4710	—	—	0.97	—	—	—
$2p_{10}-5d_5$	—	4709		—		—	—	
$2p_{10}-5d_3$	—	4704	—	—	0.93	—	—	—

a = Pure Neon—Capillary tube—Ordinary discharge.*b* = Trace of argon in 25 mm. Neon—Wide bore tube—Uncondensed discharge.*c* = " " " " Mild condensed discharge.*b'* = Pure Neon - Wide bore tube—25 mm. pressure (Table IV.).

admixture to account for the observed values. Taking the case of the s_3 group, which is critical, Table V. shows us that while a trace of hydrogen ($H_a=1.37$) gives an intensity displacement to the shorter wave-lengths, a large quantity ($H_a = 691$) reverses this. It is a matter of opinion which of these extremes the present case ($H_a=12.95$) resembles the more closely, and upon the discrimination depends the estimation of the effect of a trace of argon. It is clear that much more extensive and accurate work will be required to differentiate between the various effects.

It is perhaps worth mentioning that under the conditions of column (b) no argon lines appeared, but with the mild condensed discharge of column (c) most of the strongest lines of "red" argon were recorded, together with $H_a(12.95)$, $H_\beta(5.02)$, $H_\gamma(2.04)$.

Table VII. records the intensities of Neon lines radiated from a trace of Neon mixed with 25 mm. of helium in a wide bore tube. The light of the uncondensed discharge is a soft red colour, the greater part being due to Neon, although the strongest helium lines are visible. A mild condensed discharge yields a very intense yellow light, a very large number of sharp and diffuse lines of Neon now being radiated, together with the complete arc spectrum of helium (strongly) and a few of the helium bands. In the former case H_a has a strength of 1.7, in the latter case of 320. It was felt that it would serve no useful purpose at present to give under the respective columns of Table VII. a complete record of these lines. The record has therefore been limited to those lines which have been recorded in previous tables. The intensities of lines in the extreme red, such as $\lambda\lambda 7245$ and 7032 are of course subject to considerable errors owing to the comparative insensitivity of the photographic plate in that neighbourhood. No useful purpose would seem to be served at present by discussing the detail of Table VII., as there are numerous exceptions to any rules that can be framed. There seems to be a tendency to displacement of the energy to the shorter wave-lengths. Among the lines of exceptional variation are $\lambda\lambda 6217, 6074, 5975$, and 5852 .

The recorded results, however, indicate very considerable intensity variations, particularly with the sharp and diffuse lines. This is of quite a different order to the effect on the principal lines; and it should, for example, be possible to apply this test of the degree of enhancement in the presence of high pressure helium to separate a complex spectrum into principal and subsidiary lines.

TABLE VII.

Trace of Neon in 25 mm. Helium.

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .
$1\cdot5s_5-2p_n$	9	6402	100	100	100	1.000	1.000
	8	6334	41.4	50.7	48.1	1.225	1.162
	7	6217	14.5	26.1	27.6	1.800	1.903
	6	6143	34.5	49.2	43.0	1.426	1.246
	5	5975	6.52	15.0	29.6	2.301	4.540
	4	5945	19.2	24.1	26.4	1.255	1.375
	2	5882	12.5	43.4*	433*	3.472	34.64
$1\cdot5s_4-2p_n$	10	7245	84.3	345	320	4.093	3.796
	8	6506	61.4	112	95.9	1.824	1.562
	7	6383	47.2	100	91.2	2.119	1.932
	6	6305	17.1	28.4	37.7	2.246	2.205
	5	6128	—	—	—	—	—
	4	6096	24.1	48.0	42.1	1.992	1.747
	3	6074	19.4	33.7	27.2	1.737	1.402
	2	6030	7.16	18.6	19.7	2.598	2.751
	1	5400	1.65	1.28	4.35	0.776	2.636
$1\cdot5s_3-2p_n$	10	7032	127	380	411	2.992	3.236
	7	6533	27.3	39.3	74.3	1.440	2.722
	5	6266	22.6	39.2	41.5	1.735	1.836
	2	6163	14.6	41.1	37.7	2.815	2.582
$1\cdot5s_2-2p_n$	6	6929	80.9	145	225	1.792	2.781
	5	6717	45.4	85.3	134	1.879	2.952
	4	6678	59.1	110	432†	1.861	7.310
	2	6599	35.0	88.5	109	2.529	3.114
	1	5852	40.9	50.2	108	1.227	2.641
$2p_9-3\cdot5s_5$	—	6182	0.79	13.2	18.8	15.71	23.80
$2p_4-3\cdot5s_1$	—	5902	1.07	4.75	24.7	4.439	23.08
$2p_6-4d_4$	—	5991	} 0.45	3.46	9.89	7.689	21.98
$2p_6-4d_3$	—	5988					
$2p_3-4d_4$	—	5820	1.12	9.72	27.1	8.679	24.20
$2p_9-4d_4$	—	5764	1.76	17.0	53.4	9.660	30.34
$2p_{10}-4d_6$	—	5343	} 1.06	10.7	30.2	10.09	28.49
$2p_{10}-4d_5$	—	5341					
$2p_{10}-4d_3$	—	5330	0.96	8.63	26.7	8.990	27.81

a = Pure Neon—Capillary tube—Ordinary discharge.*b* = Trace of Neon in 25 mm. helium—Uncondensed discharge.*c* = „ „ „ Mild condensed discharge.* Helium line λ 5875 superposed.† „ „ λ 6678 „

It is perhaps appropriate to mention here that a noticeable intensity change induced by helium in a Neon doublet $\lambda\lambda$ 743.78, 735.95 has been recorded by Lyman and Saunders‡.

‡ 'Nature,' vol. cxvi. p. 358 (1925).

Ordinarily the more refrangible component is the stronger, whereas the reverse is true when the pair are developed in high pressure helium.

TABLE VIII.
Effect of admixture of CO₂.

Series.	<i>n</i> .	Wave-length.	(<i>a</i>).	(<i>b</i>).	(<i>c</i>).	<i>b/a</i> .	<i>c/a</i> .
1·5 <i>s</i> ₅ —2 <i>p</i> _{<i>n</i>}	9	6402	100	100	100	1·000	1·000
	8	6334	42·6	46·8	38·0	1·098	0·892
	7	6217	16·7	15·7	9·56	0·941	0·572
	6	6143	44·8	35·7	46·4	0·797	1·036
	5	5975	5·89	5·73	7·59	0·973	1·289
	4	5945	19·2	17·0	24·5	0·887	1·276
	2	5882	12·5	10·4	13·3	0·833	1·062
1·5 <i>s</i> ₄ —2 <i>p</i> _{<i>n</i>}	10	7245	—	16·4	—	—	—
	8	6506	67·9	77·0	101	1·134	1·493
	7	6383	67·3	59·9	73·5	0·890	1·092
	6	6305	15·8	17·9	15·6	1·133	0·984
	5	6128	—	—	—	—	—
	4	6096	28·3	21·1	36·1	0·747	1·277
	3	6074	18·3	16·1	23·2	0·880	1·268
	2	6030	7·23	6·77	7·78	0·937	1·076
	1	5400	—	—	6·95	—	—
1·5 <i>s</i> ₃ —2 <i>p</i> _{<i>n</i>}	10	7032	270	258	237	0·956	0·878
	7	6533	36·3	46·4	37·9	1·278	1·043
	5	6266	29·4	26·5	32·5	0·901	1·105
	2	6163	16·3	15·4	17·1	0·942	1·051
1·5 <i>s</i> ₂ —2 <i>p</i> _{<i>n</i>}	6	6929	93·4	110	168	1·175	1·799
	5	6717	58·6	65·2	95·2	1·113	1·624
	4	6678	75·7	81·8	145	1·081	1·917
	2	6599	44·8	48·7	68·9	1·087	1·538
	1	5852	19·3	22·0	193	1·140	10·00
2 <i>p</i> ₄ —3·5 <i>s</i> ₁	—	5902	—	0·40	3·25	—	—
2 <i>p</i> ₃ —4 <i>d</i> ₄	—	5820	—	—	3·67	—	—
2 <i>p</i> ₃ —4 <i>d</i> ₄	—	5764	—	0·59	5·31	—	—

a = Pure Neon—Capillary tube, 25 mm. pressure—Uncondensed discharge.
(Table III. (*b*).)

b = High pressure Neon and CO₂—Capillary tube.

c = " " " Cathode glow.

The data of Table VIII. were obtained from a tube consisting of a bulb having a large flat cathode in it, while a capillary portion was joined on to this bulb. The tube was filled with Neon to a pressure of about 25 mm. and possessed a side bulb of magnesite, by means of which CO₂ could be admitted as desired. The admission of the latter to a pressure of some mm. caused the cathode glow to contract to a

thin bright yellow layer about 1 mm. in breadth. The results of an "end-on" photograph of this are given in column (c), while column (b) gives the light from the capillary under these conditions. The outstanding feature of the spectrum of the cathode glow is the line $\lambda 5852$, which has a ten-fold enhancement, and gives the glow its characteristic bright yellow colour.

TABLE IX.

Intensities at various distances from the Cathode.

Series.	<i>n</i> .	Wave-length.	0 mm.	1 mm.	2 mm.	3 mm.	4 mm.	5 mm.
$1\cdot5s_5-2p_n$	9	6402	100	108	113	121	114	82.0
	8	6334	23.0	24.6	34.4	39.8	25.6	20.4
	6	6143	35.1	36.7	52.0	54.9	38.3	31.2
	4	5945	18.2	16.7	24.8	23.0	16.6	12.4
	2	5832	11.9	10.3	12.9	15.5	12.4	5.09*
$1\cdot5s_4-2p_n$	8	6506	57.0	64.6	91.8	102	71.1	53.9
	7	6383	31.1	27.9	40.9	45.7	29.5	22.3
	5	6305	8.20	4.64*	10.8	11.2	4.64*	4.64*
	4	6096	23.4	21.3	35.8	36.7	26.6	18.6
	3	6074	16.5	14.9	21.6	21.8	15.3	12.2
$1\cdot5s_3-2p_n$	10	7032	199	227	284	316	258	137*
	5	6266	16.5	18.7	26.2	26.8	18.3	13.8
	2	6163	9.35	11.4	14.8	14.5	10.6	7.17
$1\cdot5s_2-2p_n$	6	6929	205	240	318	406	257	190
	5	6717	46.2	50.4	77.1	83.9	54.2	41.3
	4	6678	76.8	104	108	104	78.1	73.3
	2	6599	17.7	22.2	24.6	28.6	22.0	10.8*
	1	5852	86.9	101	164	184	112	67.0

* These lines were not visible. The values tabulated are absolute intensities corresponding to a photographic intensity = 1 in each case (*i. e.* just visible).

We have also made a study of the distribution of intensity in the spectrum of neon, as a function of the distance from a flat cathode, similar to work done by Merton and Nicholson (*loc. cit.*). The pressure of gas was such as to give a dark space of about 1 mm. The curves representing the intensity of emission as a function of distance are somewhat similar for the various lines, though the amplitude variations of the curves differ. In most cases the maximum intensity of emission was about 2.5 mm. from the cathode. We have

not thought it desirable to enter into a fuller discussion of these results until similar information for a number of sharp and diffuse lines is available.

November 27th, 1925.

DESCRIPTION OF PLATE.

1. Positive crater of the carbon arc with "ordinary" Neon spectrum in juxtaposition.
2. Mild condensed discharge through a trace of Neon in high pressure helium. Wide bore tube. (*Vide* Table VII.)
- 3a. Uncondensed discharge through a trace of Neon in high pressure helium. Wide bore tube. (*Vide* Table VII.)
- 3b. "Ordinary" Neon spectrum. Plücker tube. Capillary bore. Pressure corresponding to about 1 mm. dark space.
- 4a. Ordinary spectrum of pure Neon as above. (*Vide* Table V.)
- 4b. Same as above plus a trace of hydrogen.
- 4c. Same as above plus a quantity of hydrogen (say 2 or 3 mm.).
- 5a. Ordinary spectrum of pure Neon as above. (*Vide* Table IV.)
- 5b. Neon at 25 mm. pressure in wide bore tube.
- 5c. Neon at very low pressure in wide bore tube. (Fluorescence of glass visible: say about 1/100 mm.)

LIII. *Note on the Structure of Cadmium and Zinc Resonance Lines.* By Prof. R. W. WOOD*.

[Plate XI.]

THE structure of the 2536 line of mercury was reported in this Journal (vol. i. p 762, 1925), but the other, resonance line 1849 has not yet been examined. A possible method might be to use an echelon by reflexion, mounting the entire apparatus *in vacuo*. I have examined the mercury green line in this way, and found the resolution of the companion lines fairly good. Since the publication of the paper referred to above I have examined the fine structure of the $1S-2p_2$ and $1S-2P$, the analogous lines of cadmium and zinc.

The source of light in each case was a metallic arc in a tube of fused quartz furnished with an anode of tungsten wire. The tube was continuously exhausted by a mercury-vapour pump during its operation, and the cathode bulb, which contained the metal, was immersed in water.

The fine structure of the lines was photographed with the

* Communicated by the Author.

two quartz Lummer-Gehrcke plates described in the earlier paper, but in this case the plates were employed in succession, and not crossed. The structure of the 2536 Hg-line, as was shown in the earlier paper, is less complicated than the structure figured by Nagaoka, whose photographs were complicated by absorption. It consists of five lines of nearly equal intensity and almost equidistant. The corresponding lines of cadmium and zinc showed a much simpler structure, as was to be expected.

The fringes formed by the interference plates were focussed on the slit of a small quartz spectrograph by means of a quartz-fluorite objective of 40 cm. focus. The structure of the cadmium lines obtained in this way is shown on Plate XI., the photographs being reproduced as negatives. Figs. 1 and 2 show the 2288 line obtained with the thin and thick Lummer plates respectively. The constants of the two plates will be found in the paper following the present note. It was at first thought that the line might be single, but strongly reversed. This, however, is not the case, as the appearance is the same with the discharge pressed against the front and back wall of the tube by a magnetic field. In the latter case the absorption is very strong, but the lines are merely weakened as a whole, with no trace of reversal down the centre, as was the case with the five components of Hg 2536. The wave-length separation of the lines was computed by Dr. McNair, who extended the work to the other lines of the spectrum. The values found were $\cdot000$ and $\cdot021$ (or $-\cdot017$). In the case of 3261, which is analogous to Hg 2536 ($1S-2p_2$), we have a strong and easily reversed line accompanied by a faint companion on the short wave-length side: separation $\cdot000$ and $-\cdot019$. Figs. 3 and 5 show the line as given by the thin and thick plates, and fig. 5 shows the main line so strongly reversed (by driving the discharge against the back wall) that the components of the reversed line are not much more intense than the faint companion. In the case of zinc 2138.6 $1S-2P$ was found to be double, like Cd 2288, while 3075.9 $1S-2p_2$ was single.

LIV. *The Fine Structure of Certain Lines and Energy Levels of Cadmium.* By WALTER A. MACNAIR, *National Research Fellow* *.

[Plate XII.]

PART I.

RECENT attempts have been made to obtain the fine structure of the energy levels of certain elements from the fine structure of their spectrum lines by Ruark, Mohler and Chenault †, by Ruark and Chenault ‡, and by Joos §. It is evident that if anything like a complete fine structure energy level diagram of any one element is to be constructed the fine structure of many lines of that element must be obtained. The work reported here is the beginning of an attempt to obtain the fine structure of the spectrum lines of the elements in the zinc-cadmium group, and also the structure of their energy levels.

The light from a cadmium arc was passed through a crystalline quartz lens screened by a vertical slit about a centimetre wide and ten centimetres long. At the focus of the lens the light was passed through a small quartz double-image prism and then into a quartz Lummer-Gehrcke plate. The fringe systems of all of the spectrum lines were focussed simultaneously (using the beam polarized with the electric vector parallel to the parallel surfaces of the Lummer-Gehrcke plate) by a quartz-fluorite achromatic lens on the slit of a spectrograph, so that a plate exposed in the spectrograph gave the fine structure of all of the lines at once. Two different quartz spectrographs and two different grating spectrographs were used at various times during the investigation. The technique of using Lummer-Gehrcke plates in the ultra-violet region has been described by Professor Wood in the *Philosophical Magazine* ||.

The cadmium arc was made of quartz tubing of 8 mm. inside diameter. The tungsten-wire anode was sealed in at one end by means of hard glass and intermediate glasses, and the metallic cadmium cathode, which was about 15 centimetres from the end of the tungsten wire, was kept cool by dipping the cathode end of the arc in running

* Communicated by Prof. R. W. Wood.

† 'Nature,' cxiv. p. 575 (1924).

‡ *Phil. Mag.* l. p. 937 (1925).

§ *Phys. Zeits.* xxvi. No. 10 (1925).

|| Wood, R. W., *Phil. Mag.* l. pp. 762-763 (1925).

water. The light from the side of the arc several centimetres from the cathode was observed.

Two quartz Lummer-Gehrcke plates made by Adam Hilger & Co. were used. One is 4.40 mm. thick and 130 mm. long, and the other is 6.55 mm. thick and 200 mm. long. From these dimensions and the optical constants of quartz the distance in A.U. between orders of the fringe system due to a plate can be calculated, as shown by Nagaoka* and by Simeon†. The following table gives the values calculated for various wave-lengths:—

Wave length.	A.U. between consecutive orders.	
	4.40 mm. plate.	6.55 mm. plate.
2000 A.U.	.028	.019
2500 „	.049	.033
3000 „	.076	.051
3500 „	.109	.073
4000 „	.145	.097
4500 „	.186	.125
5000 „	.230	.154
5500 „	.282	.189
6000 „	.341	.229

By comparing three photographs of the fine structure—one taken when a magnetic field forced the arc discharge against the side of the tube nearest the analysing apparatus, another when the discharge was against the opposite side, and the third when no magnetic field was used—it is seen that the main component of each of the following subordinate series lines is reversed under the last two conditions: 5085.9, 3080.9, 3610.5, 3403.6 (the reversal being more complete when the discharge is against the far side of the tube). The other components of these lines and all the components of the other lines observed did not reverse. Professor Wood has reported the behaviour of the resonance lines elsewhere in this journal.

The position of the fringes of each line was determined to .01 mm. by observing the plates on a dividing engine. Usually the position of the fringes in about ten consecutive orders was recorded. The method of computing the separation of two components in A.U. can be explained by referring to fig. 1.

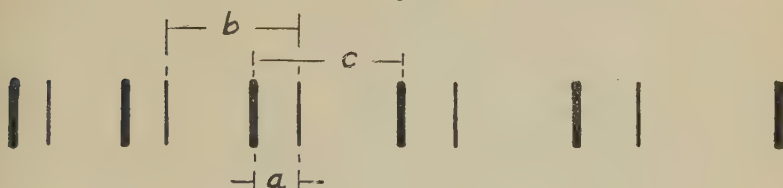
* Proc. Tokyo Math.-Phys. Soc. viii. (Ser. 2) p. 296.

† Journ. Scientific Inst. i. No. 10 (July 1924).

The average of the distances b and c is taken as the separation of orders, in millimetres. Then $\frac{a}{\frac{b+c}{2}}$ times the

separation of orders in A.U., as taken from the curves drawn from Table I., gives the separation of components in A.U. The weaker component in fig. 1 is of shorter wave-length than the main component if the pair of components separated by a millimetres is taken as a complete order, as is assumed to be the case in the above illustration. That is, the shorter wave-length components appear on that side of the main component toward which the separation of orders (in millimetres) increases. In deciding to which main component any particular satellite

Fig. 1.



belongs, no ambiguity remains after comparing the interference patterns due to both Lummer-Gehrcke plates, as will be seen by inspecting the reproductions (fig. 2, Pl. XII.) and remembering that the thicker plate has about one and one-half times the dispersion of the thinner one. This simple method is possible when dealing with elements like cadmium, the lines of which have a fine structure which is not spread over such a range as to intermix the orders due to the interferometer so badly that they cannot be easily separated. In but two cases of all with which we are here concerned have the components of two different orders overlapped; these will be pointed out in some remarks on the reproductions.

There has been some recent discussion by E. Gehrcke* and P. H. Van Cittert† as to the accuracy and reliability of results obtained with Lummer-Gehrcke plates. G. Hansen‡ has also discussed the question. Since cadmium is much

* *Ann. d. Phys.* lxxviii. p. 461 (1925).

† *Ibid.* lxxvii. p. 372 (1925); lxxix. p. 94 (1926).

‡ *Ibid.* lxxviii. p. 558 (1925).

heavier than hydrogen, the Lummer-Gehrcke plate fringes were naturally much narrower for the former element, which eliminated part of the difficulties Hansen had to contend with. The accuracy of the work reported here may be judged by inspecting Table II., where the observations

TABLE II.

Fine Structure of the 5085·9, 4799·9, and 4678·2 Lines of Cadmium.

5085·9 $2p_1-2s$.				
+·076 ($\frac{1}{2}$);	·000 (1);	—·026 ($\frac{1}{8}$?)		Janitzki ¹ .
+·076 (2);	·000 (10);	—·026 (1)		Wali-Mohammad ² .
+·077 (2);	·000 (10);	—·025 (2)		Takamine ³ .
+·077 (7);	·000 (10);	—·025 (4)		MacNair.
4799·9 $2p_2-2s$.				
+·058 ($\frac{1}{2}$);	·000 (1);	—·034 ($\frac{1}{2}$);	·081 ($\frac{1}{5}$)	Janitzki.
+·058 (6);	·000 (10);	—·034 (3);	·081 (6)	Wali-Mohammad.
+·059 (3);	·000 (10);	—·033 (1);	·080 (2)	Takamine.
+·058 (6);	·000 (10);	—·034 (3);	·081 (3)	MacNair.
4678·2 $2p_3-2s$.				
+·030 ($\frac{1}{2}$);	·000 (1);	—·056 ($\frac{1}{6}$)		Janitzki.
+·031 (3);	·000 (10);	—·056 (6)		Wali-Mohammad.
+·031 (4);	·000 (10);	—·057 (2)		Takamine.
+·031 (8);	·000 (10);	—·056 (4)		MacNair.

¹ Janitzka, *Ann. d. Phys.* xix. p. 36 (1906); xxix. p. 833 (1909).

² Wali-Mohammad, *Ann. d. Phys.* xxxix. p. 225 (1912).

³ Takamine, *Proc. Tokyo Math.-Phys. Soc.* viii. p. 51 (1915).

of the fine structure of three lines by four independent observers may be compared. The greatest difference in the observed positions of any one component is ·001 A.U. Also by inspecting Table III., where the fine structure computed from the measurements on the fringe system due to each plate is reported separately. Here the greatest difference in the computed positions of any one component is ·002 A.U., so that the final results reported are probably correct to ·001 A.U. In four cases the thin plate did not resolve a close satellite sufficiently to allow a reliable measurement. In these cases the results for the thick plate alone are reported.

TABLE III.

Fine Structure of Cadmium Lines. (MacNair.)

[In this Table the main component ·000 (10) has been omitted in each line.]

Line 3252·5:	$2p_1-3s$.	
Thick Plate	+·031;	—·010
Thin Plate	+·031;	—
$\Delta \lambda$ (Intensity)...	+·031 (2);	—·010 (3)
$\Delta \nu$ (cm. ⁻¹)	—·293;	+·095

Line 3133·2 :	$2p_2-3s.$
+·024 ;	—·012 ; —·032
+·025 ;	— ; —·033
+·024 (1) ;	—·012 (1) ; —·033 (1)
—·245 ;	+·122 ; +·337

Line 3080·9 :	$2p_3-3s.$
+·012 ;	—·024
+·013 ;	—·022
+·013 (3) ;	—·023 (2)
—·137 ;	+·242

Line 3614·4 :	$2p_1-3d''.$
+·037 ;	—·023
+·038 ;	—·023
+·037 (2) ;	—·023 (4)
—·283 ;	+·176

Line 3610·5 :	$2p_1-3d.$
	—·035
	—·037
	—·036 (3)
	+·276

Line 3466·2 :	$2p_2-3d'.$
+·031 ;	—·016
+·031 ;	—·015
+·031 (3) ;	—·015 (5)
—·258 ;	+·125

Line 3403·6 :	$2p_3-3d''.$
	+·017
	+·017
	+·017 (5)
	—·147

Line 2980·6 :	$2p_1-4d.$
	—·025
	—·027
	—·026 (1)
	+·293

Line 2881·2 :	$2p_2-4d''.$
+·021 ;	—·011
+·022 ;	—·010
+·021 (1) ;	—·010 (5)
—·253 ;	+·120

Line 2836·9 :	$2p_3-4d''.$
	+·012
	+·011
	+·011 (4)
	—·136

Line 4413·1 :	$2p_2-3S.$
+·028 ;	—·015
+·028 ;	—
+·028 (1) ;	—·015 (3)
—·144 ;	+·077

Line 3499·9 :	$2p_2-3D.$
+·018 ;	—·010
+·016 ;	—
+·017 (2) ;	—·010 (4)
—·139 ;	+·082

Note.—Many times during this investigation the fringes of 6438·5 were beautifully clear and distinct. Several times this line was inspected with care, and it always appeared single.

The intensity estimates were made by comparing, under a low-power binocular micro-scope, the density of the components with the densities of a series of spectrograms taken with a slit-width about equal to the width of a fringe and with exposure times varying from 1 to 10. The density of the lines of the spectrogram varied over such a range that in most cases a line could be found in the spectrogram of exposure 10 which was of the same density as the main component of the cadmium line under observation. In this case the number to be assigned to the intensity of a weaker component was found with ease. While these estimates represent fairly well the relative intensities of the components as the light strikes the photographic plate, it must be borne in mind that the actual relative emission intensities may be something quite different because of the strong absorption of the subordinate series lines and the incipient reversal of the strong component of each.

In the following tables a component marked $+0.77(2)$ is a component which is 0.77 A.U. away from and on the long wave-length side of the strongest component of the line observed and has an intensity of 2 as compared with 10, the intensity assigned to the strongest component.

Table IV. has been added for the sake of completeness and to have the data handy for considerations taken up in Part II.

TABLE IV.
Fine Structure of other Cadmium Lines.

Wave-length.	Classification.	Remarks.
3261.0	1S-2 p_2	Double, $\Delta\lambda - 0.19(2)$, $\Delta\nu + 179$. Wood ¹ .
2288.0	1S-2P	Double, $\Delta\lambda + 0.21(10)$, $\Delta\nu - 400$. Wood ¹ . or $-0.17(10)$ or $+324$.
6438.5	3P-3D	Single. Michelson, Fabry and Perot, Hamy ² , Janitzki ³ .
6325.2	2P-3d'	Double (no separation given). Hamy ² , Janitzki ³ .
5154.7	2P-3S	Single. Hamy ² , Janitzki ³ .
4664.5	2P-4D	Single. Hamy ² , Janitzki ³ .

¹ Wood, *suprà*, p. 611.

² Hamy, *C. R. cxxx.* p. 489 (1900).

³ Janitzki, *Ann. d. Phys.* xix. p. 36 (1906); xxix. p. 833 (1909).

Remarks on Reproductions. (Fig. 2, Pl. XII.)

In preparing the reproductions an attempt has been made to show the existence and position of each component; consequently the contrast has been developed as much as

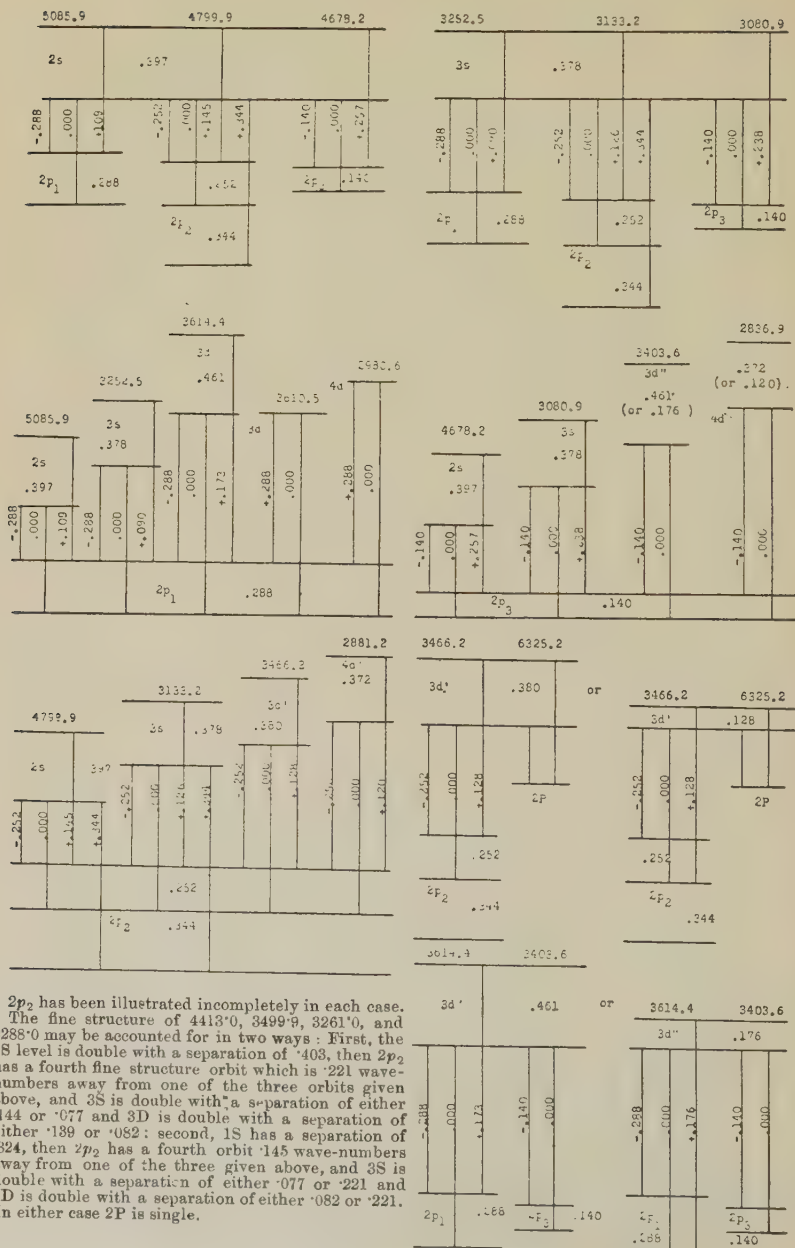
possible, so that no great importance can be given the relative intensities of the fringes as reproduced.

- 5085·9 (Thick plate). The main component appears reversed in two orders. The other lines appearing are 4799·9 and 4678·2.
- 4799·9 (Thick plate). Two components shown by the thin plate are overlapped and shown as one fringe by the thick plate. 4678·2 appears also.
- 4678·2 (Thin plate). 4799·9 appears also.
- 4413·1 (Thin plate). The $-.015$ component is unresolved from the main component.
- 3614·4 (Thick plate). 3610·5 and 3612·9 appear here very much over-exposed.
- (Thin plate). 3610·5 and 3612·9 have been partially cut away.
- 3610·5 (Thin plate). 3612·9 and 3614·4 appear also.
- (Thick plate). 3612·9 and 3614·4 have been cut away.
- 3499·9 (Thin plate). The $-.010$ component is unresolved from the main component.
- 3466·2 (Thick plate). 3467·8 appears also.
- (Thin plate). 3467·8 has been partially cut away.
- 3252·5 (Thin plate). The edge of 3261·0 appears.
- 3133·2. Two components shown by the thin plate are overlapped and shown as one fringe by the thick plate.
- 3080·9 (Thin plate). 3138·2 appears also.
- 2980·6 (Thin plate). 2981·3 and 2981·9 appear also.
- (Thick plate). 2981·3 and 2981·9 have been cut away.
- 2881·3. The reproduction of this line is not as satisfactory as the others, so it has been omitted.

PART II.

An attempt has been made to account for all the observed fine structure of the lines by assigning a certain fine structure to each level. Fig. 3 shows the result of such an attempt. The separations of the fine structure levels of any one level have been adjusted from the separations observed in all the lines starting or ending on that level. The separations are expressed in wave-numbers to the third decimal place, which, in most cases, implies an accuracy higher than that actually attained. The separations assigned to the p levels are slightly different from those assigned by Joos (*loc. cit.*), and $2p_2$ is more complex. 3403·6 may originate from the upper $3d''$ level and 2836·9 from the upper $4d''$ level. $4D$ and $4S$ need not be anything but single, though they may be double with a selection principle operating. Numbers can be assigned to the fine structure orbits, and an arbitrary selection principle stated so as to allow only those lines which appear.

Fig. 3.



$2p_2$ has been illustrated incompletely in each case. The fine structure of 4413.0, 3499.9, 3261.0, and 2288.0 may be accounted for in two ways: First, the 1S level is double with a separation of .403, then $2p_2$ has a fourth fine structure orbit which is .221 wave-numbers away from one of the three orbits given above, and 3S is double with a separation of either .144 or .077 and 3D is double with a separation of .324, then $2p_2$ has a fourth orbit .145 wave-numbers away from one of the three given above, and 3S is double with a separation of either .077 or .221 and 3D is double with a separation of either .082 or .221. In either case 2P is single.

There may be some significance in the fact that certain sets of orbits are similar; for instance, $2s$ and $3s$, $1S$, $3S$ and possibly $4S$, $3d$ and $4d$, $3d''$ and $4d''$. It should be noted also that $2p_2$ is without doubt much more complicated than either $2p_1$ or $2p_3$.

The fine structure of the cadmium lines which has been observed may be almost as nicely accounted for by quite a different arrangement of the fine structure of the orbits. In this arrangement the following orbits are the same as in the previous arrangement: $2s$, $2p_1$, $2p_3$, $1S$ (double, with separation of either $\cdot400$ or $\cdot324$), $3d$, $4d$, and $3d''$ (double, with separations of either $\cdot461$ or $\cdot176$). The following orbits are single: $3d'$, $4d''$, $3S$, $4S$, $3D$, and $4D$. The $3s$ orbit is double with a separation of $\cdot243$, and $2p_2$ has five fine structure orbits separated as follows (starting with the separation of the highest two): $\cdot254$, $\cdot123$, $\cdot141$, $\cdot080$. With this set of fine structure orbits it is possible to account for all the components of the fine structure of the lines observed, except the double structure of $6325\cdot2$ and the $+0\cdot95$ component of $3252\cdot5$. Other possible objections may be that $2p_2$ is relatively too complicated, and the $+0\cdot176$ component of $3614\cdot4$ is accounted for by making $3d''$ double while the other higher orbits are single.

I am greatly indebted to Professor R. W. Wood, with whom I worked continuously for three weeks in order to learn the technique of the Lummer-Gehrcke plate, and who has given many suggestions concerning experimental procedure during the progress of the work.

The Johns Hopkins University,
Baltimore, Md.
June 18, 1926.

LV. *Note on some Observations of the Nitrogen Afterglow Spectra.* By R. C. JOHNSON, B.A., Ph.D., and H. G. JENKINS, B.Sc. (Queen's University, Belfast)*.

Introduction.

IT is very remarkable that there are so few molecules capable of yielding an afterglow emission. The familiar nitrogen afterglow is of course outstanding among these, and its nature and properties are well known to us through

* Communicated by the Authors.

the work of Lewis *, Rayleigh †, and others on the experimental side, and that of Birge ‡ and many others from a theoretical standpoint. The spectrum of the nitrogen afterglow, consisting of the so-called α -, β -, and γ -groups, is partly in the visible region and partly in the ultra-violet. To be more precise, the group, which we believe originates from a metastable N_2 molecule, lies in the red, yellow, and green; the other groups, originating from a metastable NO molecule, are chiefly in the ultra-violet. It seems conceivable, therefore, that many molecules may radiate afterglows lying entirely in the ultra-violet, and unsuspected through having no visual accompaniment. We have made a systematic search in a number of typical cases, but with negative results. At the same time we have used the method described below to make an extensive series of observations of the nitrogen afterglow, and some of the facts—though mostly familiar through Rayleigh's work—were felt to be worth recording, especially as they have been the subject of controversy.

Experimental.

We have used a method the same in principle as that described by Lewis. An interrupter of the magnetic type was inserted in the primary circuit of the induction-coil. The interrupter used had three solenoidal coils corresponding to three prongs disposed at 120° , which made periodic contact with a mercury surface. A disk consisting of three sections of 60° angle was fixed to the axle of the interrupter and "tuned" so that observation of the light from the tube was possible only at the intervals when the discharge current was off (see fig. 1).

This method was found excellent for a search for afterglows in the ultra-violet, the light of the discharge-tube being photographed by a quartz spectrograph after passing through the disk. It also has a great many advantages over the stream method.

- (1) A discharge-tube of practically any length may be used, and a light-source of high intrinsic value is thus available. It is suggested that this method will be found excellent when grating photography of the β -group for the purpose of fine-structure analysis is attempted.

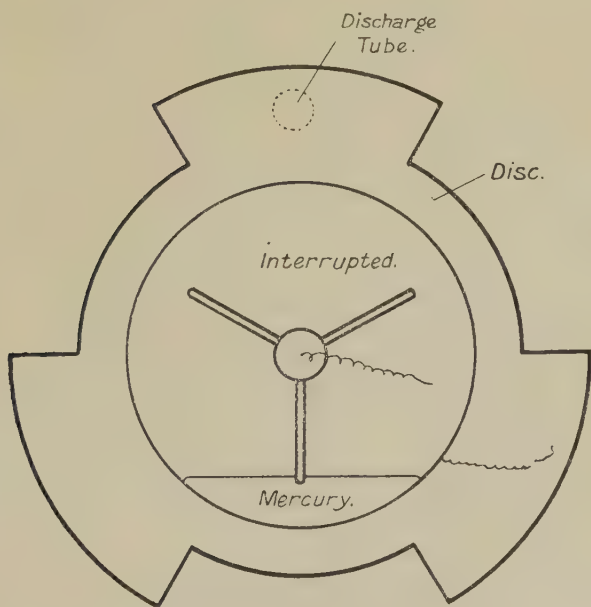
* Ast. Journ. vol. xx. p. 50 (1904). Phil. Mag. (6) vol. xxv. p. 826 (1913).

† Proc. Roy. Soc. A, vol. lxxxv. p. 377 (1911); vol. lxxxvi. p. 105 (1912); vol. xciii. p. 254 (1917), etc.

‡ 'Nature,' Nov. (1924). Ast. Journ. vol. lv. p. 273 (1922). Phys. Rev. vol. xxiii. p. 295 (1924), etc.

- (2) It permits of the detection and photography of afterglows of short duration.
- (3) By adjustment of the speed of the disk and the use of suitably placed sectors, it should be possible to examine the afterglow spectrum at any particular time after its production. (This may be of some importance—as one of us has pointed out (*Phil. Mag.* vol. xlviii. p. 1069, 1924)—in connexion with the theory of the α -group “selection.”)

Fig. 1.



The Nitrogen Afterglow.

The disk method permits of no possibility of stray light from the discharge giving spurious results, and definitely confirms Rayleigh's observations of the presence of many of the groups of the first positive band spectrum in addition to the enhanced “selection.” It is equally certain that the second positive nitrogen bands are no part of the afterglow spectrum. In all our experiments we used glass tubes of the H type fitted with quartz window and side bulbs containing KOH and P_2O_5 . Under these circumstances it was found that while the β - and γ -groups appeared along with

the α -group immediately after having filled the tube, no trace of them was found after the discharge had passed for two or three hours, the oxygen impurity having presumably been removed as oxides of nitrogen into the potash. Such a tube was prepared and fitted with a side bulb containing KMnO_4 for the purpose of admitting oxygen. By admission of oxygen into the pure nitrogen, as produced above, the β - and γ -groups were stimulated with great strength. We found them of maximum strength when the α -group had been suppressed, and only a faint blue light (due to the less refrangible members of the β -group) was visible in the tube. Addition of a large amount of oxygen then produces the curious afterglow with a greenish-yellow continuous spectrum referred to by Rayleigh.

We have found that the best conditions for its production are a little nitrogen in a large quantity of oxygen. Photographs of its spectrum yield nothing notable except the continuous spectrum above $\lambda 4300$. The mercury line $\lambda 2536$ was notably absent in the presence of this spectrum, although it had been conspicuously strong a short time before in the nitrogen afterglow. This would seem to place an upper limit of 4.86 volts to the energy with which this curious afterglow molecule is loaded.

In view of Rayleigh's observations* on the modifications of the α -group in the presence of the inert gases, we have used the disk method to examine the β - and γ -groups under these circumstances. We have examined the nitrogen afterglow produced in the presence of high-pressure helium and argon, but there is no apparent change in the intensity distribution.

The Cyanogen "Tail" Bands.

On several of our plates a system of bands degraded to the red and described by Rayleigh† as "Tails" of the violet CN bands appears. Their presence was due to a trace of carbon contamination in the tube. Our observations of the intensity variations of the system with the CN bands leave no doubt as to its connexion with them.

In view of our knowledge of the spectra which originate from one-valence electron emitters of which CN is the prototype, it was thought of some importance to examine this system more closely to see whether there was any quantum theory relation between it and the two familiar

* Proc. Roy. Soc. A, vol. cii. p. 453 (1923).

† Proc. Roy. Soc. A, vol. lxxxvi. p. 115 (1912).

spectra of CN. Table I. gives wave-length measurements of the bands on our plates, which are possibly correct to

TABLE I.

Int.	λ (IA).	Wave-no. <i>in vacuo.</i>	λ (IA) King.	Wave-no.	n' .	n'' .
c.	4133.1	24188	—	—	11	13
3	4079.3	24507	—	—	10	12
5	4030.0	24807	—	—	9	11
8	3986.3	25079	3984.78	25088.4	8	10
8	3948.4	25319	3944.76	25342.9	7	9
8	3914.5	25539	3910.30	25566.3	6	8
7	3889.3	25704	—	—	5	7
v.c.	3869.8	25834	—	—	4	6
2	3693.4	27068	—	—	7	8
4	3663.2	27291	3658.19	27328.2	6	7
5	3635.4	27499	3628.91	27548.7	5	6
7	3612.9	27671	3602.97	27746.5	4	5
3	3542.7	28219	—	—	9	9
6	3502.0	28547	—	—	8	8
8	3466.1	28843	3465.54	28847.3	7	7
6	3433.8	29114	3433.03	29120.5	6	6
3c	3407.2	29341	3404.90	29361.0	5	5
1	3386	29525	3380.44	29573.5	4	4
—	—	—	3360.13	29752.2	3	3
—	—	—	3340.50	29927.1	2	2
—	—	—	3322.26	30091.4	1	1
—	—	—	3296.34	30328.0	0	0
2d	3262.2	30645	—	—	7	6
0	3231.9	30933	—	—	6	5
1	3204.9	31193	3203.71	31204.8	5	4
0	3182	31417	3180.45	31433.0	4	3
—	—	—	3160.19	31634.5	3	2
—	—	—	3142.93	31808.2	2	1
—	—	—	3127.87	31961.4	1	0

about 0.5 Ångström unit for the strong heads. Micrometer settings were made on the *edge* of each band, which probably accounts for the discrepancy between King's values and our own. In addition, the intensity distribution within the bands is different for their production in active nitrogen and in the carbon arc. King's observations* were made on the carbon arc. His values also are probably in error by a few tenths of an Ångström unit, as shown by an analysis of the corresponding wave-numbers. We have assigned vibrational quantum numbers tentatively, as indicated in Table I.; but these are subject to a measure of uncertainty, and a

* Ast. Journ. vol. 14 (1901).

closer examination of the bands as produced in the carbon arc would be desirable before calculating formulæ. It will be noted that King has observed a large number of heads at the more refrangible end of two of the groups, which we have not obtained in active nitrogen. If these are definitely present and a part of the system, they correspond to transitions from and to the states of small vibrational quantum number, and the first band observed in active nitrogen, $\lambda 3182$, would be the (4, 3) band. We have assumed that they are genuine in the above assignment of (n' , n''). The distribution of energy among the vibrational states is then somewhat abnormal. The afterglow development is characterized by the absence of the initial states $n'=0, 1, 2$, and 3, and the final states $n''=0, 1$, and 2, and it is therefore notably a high temperature but non-thermal distribution. The production, under the arc conditions, of the early members of the sequences $\Delta n=0$ and $\Delta n=-1$ only ($\Delta n=n''-n'$) will then indicate, according to Lenz, comparatively little interaction between the emitting electron and the nuclear vibrations (*cf.* Mulliken's discussion of intensities in the spectra of BO, SiN, and CuI)*.

Altogether a much more critical examination of the system under arc conditions is desirable. Our analysis on the basis of available data makes it improbable, however, that it is related to either the violet or red CN systems. The possibility that it originates in ionized CN (*i.e.* CN^+) will have to be considered, though such a molecule would be of the inert gas type (*cf.* BN), and therefore difficult, if at all possible, to excite. On the other hand, CN probably has a very low ionization potential, for the initial state of the violet CN emitter is only 3.18 volts above the normal level. It is therefore not an impossible conjecture that active nitrogen may be capable of exciting CN^+ .

The β -group of the Nitrogen Afterglow.

The so-called β -group, which occurs along with the γ -group or third positive bands of nitrogen in the afterglow, has been re-measured. Some good photographs were obtained by both the disk and stream methods, and Table II. records the wave-lengths measured, together with Rayleigh and Fowler's† values. We have extended the system at the less refrangible end, and have arranged it in series,

* Phys. Rev. vol. xxv. p. 259 (1925); vol. xxvi. p. 319 (1925); vol. xxvi. p. 1 (1925).

† *Loc. cit.*

TABLE II.

λ (Å).	Int.	Wave-no.	λ (Rayleigh).	Int.
5270.1 } 5252.7 }	00	18969.7 19032.4	—	—
4912.1 } 4892.1 }	2	20352.2 20435.4	—	—
4810.0 } 4791.4 }	1	20784.2 20864.9	—	—
4589.7 } 4572.5 }	5	21781.8 21863.8	—	—
4494.8 } 4479.1 }	3	22241.7 22319.7	—	—
4401.5 } 4385.7 }	2	22713.2 22795.0	—	—
4309.7 } 4293.7 }	3	23197.0 23283.4	4312.3 4296.5	1
4303.1 } 4288.2 }	3	23232.5 23313.3	—	—
4214.9 } 4199.8 }	4	23718.7 23804.0	—	—
4127.3 } 4113.0 }	4	24222.1 24306.3	—	—
4041.2 } 4027.2 }	6	24738.2 24824.2	4042.8 4028.7	2
3962.7 } 3949.7 }	2	25228.2 25311.2	—	—
3880.7 } 3868.3 }	5	25761.3 25843.8	—	—
3800.9 } 3788.0 }	10c	26302.1 26391.7	3801.9 3789.3	4
3647.0 } 3662.4 }	Ove	27210.6 27296.7	—	—
3658.4 } 3647.0 }	4	27326.6 27412.0	—	—
3583.2 } 3571.9 }	10c	27900.1 27988.3	3584.7 3572.9	6
3456.9 } 3446.0 }	2	28919.4 29010.9	—	—
3408.5 } 3398.9 }	1c	29330.0 29412.9	—	—
3386.0 } 3375.9 }	10	29524.9 29613.3	3387.2 3376.8	9
3364.3 } 3355.2 }	0	29715.5 29796.0	—	—
3340.3 } 3330.7 }	3	29928.8 30015.1	—	—
3298.6 } 3289.7 }	0d	30307.2 30389.2	—	—

TABLE II. (*continued*.)

λ (Å).	Int.	Wave-no.	λ (Rayleigh).	Int.
3206.9 } 3197.4 }	10	31173.8 31266.4	3207.4 3198.4	10
3168.4 } 3158.6 }	3 obsc.	31552.6 31650.5	—	—
3131.1 } 3125.0 }	2	31928.4 31990.8	—	—
3042.7 } 3034.3 }	10	32856.0 32947.0	3043.2 3035.0	10
3010.7 } 3002.8 }	1	33205.2 33292.6	—	—
2950.8 } 2943.2 }	3	33879.2 33966.7	2951.2 2944.0	2
2923.6 } 2915.6 }	4 <i>d</i>	34194.4 34288.2	2923.8 2916.2	2
2892.4 } 2884.8 }	10	34563.3 34654.3	2893.0 2885.4	9
2809.5 } 2802.4 }	4	35583.1 35673.2	2809.7 2802.7	2
2786.0 } 2779.5 }	3	35883.2 35967.1	2786.5 2780.1	2
2754.2 } 2747.3 }	9	36297.5 36388.6	2754.5 2747.9	7
2731.7 } 2725.4 }	1	36596.4 36681.0	2732.2 2726.0	1
2678.7 } 2672.2 }	7	37321.2 37410.5	2678.8 2672.9	3
2626.5 } 2620.4 }	6	38062.1 38150.7	2626.9 2620.9	4
2608.3 } 2602.1 }	6	38327.7 38419.0	2608.6 2602.9	2
2557.9 } 2551.8 }	5	39082.9 39176.3	2558.0 2552.3	2
2542.2 } obsc. }	2 } — }	39324.2 —	2542.8 2537.1	1
2528.7 } 2523.2 }	0 <i>d</i>	39534.1 39620.3	—	—
—	—	—	2509.0 2503.2	1
2493.4 } 2487.8 }	7	40085.7 40184.0	2493.9 2488.3	3
2433.0 } 2427.8 }	7 <i>d</i>	41089.0 41177.0	2433.2 2428.2	3
2386.4 } 2381.5 }	1	41890.5 41977.5	2387.0 2382.3	1
2331.4 } 2326.6 }	3	42879.5 42968.0	2331.5 2326.8	2
—	—	—	2236.1 2232.2	1

assigning vibrational quantum numbers (n' , n''). The series denoted β , β_1 , β_2 , and β_3 by Rayleigh and Fowler are respectively given by $n'=0, 1, 2$, and 3 . The whole arrangement is shown in Table III. The assignment of final quantum numbers was a matter of some difficulty at first. Birge and Mulliken* have stated, however, that the β - and γ -groups have the same final electronic state—which is the normal state of the NO molecule—so that the assignment of final quantum numbers to the third positive group is of assistance. No very good measurements of this group are available, and so the system was re-measured. It has not been thought necessary to reproduce these measures here. The use of Schumann plates made the measurement of the system possible down to $\lambda 1900$, and an analysis of these values gives the band at $\lambda 2269$ as the (0, 0) band of the system. A correct assignment of quantum numbers to the β -system has therefore been possible. With only four initial states a very accurate calculation of the coefficients of n' and n'' was not possible. We find, however, that the system is fairly represented by:

$$\nu = \left. \begin{matrix} 46394.6 \\ 45485.0 \end{matrix} \right\} + (1029 n' - 7.5 n'^2) - (1889.05 n'' - 13.96 n''^2).$$

There is no doubt from our figures that the doublet separation is not constant through the spectrum. The separations for the β -series (0, n'') are a function of n'' , involving at least the first and second powers of n'' , so that the formulæ for the two heads are really different. We have, however, used the same coefficients 1889.05 and 13.96 for both heads, and also the mean value (90.4 units) of the separation in the above formulæ. The error introduced by doing this is only small.

In connexion with the energy levels of the nitric oxide molecule, an interesting letter by Dr. Spooner has recently appeared in 'Nature,' Jan. 16th, 1926. From this it is apparent that $\lambda\lambda 2269$ is the (0, 0) band of the third positive nitrogen system. In addition, the Birge-Hopfield bands in the region $\lambda\lambda 1854-1250$ are found to have their final electronic state identical with the initial state of the third positive emitter. It seems possible, therefore, that there may be another band system found in the nitrogen afterglow—in the Schumann region—having for its initial state that of the Birge-Hopfield system, and for its final state the initial state of the β -group. This possibility would be worth investigating.

* 'Nature,' p. 349, Sept. 6th, 1924.

TABLE III.

n'	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.
n''			1791.7	1763.4	1736.6	1707.4	1681.4	1652.0	1624.9	1597.3	1566.2	1541.0	1508.5	1480.7	1450.1	1429.0	1403.0
0	---	visible	(6)	(9)	(10)	(10)	(10)	(10)	(10)	(10)	(6)	(3)					
			38151	36388	34654	32947	31266	29613	27988	26392	24824	23283					
1021.5				(5)	(7)	(4)	(3)		(2)	(4)	(5)	(4)	(2)				
1	---	trace	39176	37410	35673	33967	trace	---	29011	27412	25844	24203	22795				
1007.4		(1)	(7)	(6)	(1)							(2)	(4)	(3)	(1)		
2	visible	41977	40184	38419	36681	---	---	---	---	---	---	25311	23804	22320	20865		
991.4		(3)	(7)			(3)	(4)							(3)	(5)	(2)	(00)
3	visible	42968	41177	obs.	---	35967	34288	trace	---	---	---	---	trace	23313	21864	20435	19032

For the sake of simplicity, only the more refrangible member of each doublet is given in the above table. The other heads are found in Table II.

Intensity Distribution in the β -System.

In addition to the wave-numbers, Table III. records estimated intensities. A study of these presents some very remarkable features. A discussion of the distribution of intensity among the vibrational states has been made for BO, SiN, and CuI by Mulliken*, and for the β -group and other systems by Birge*. The distribution has been studied by these and other investigators as a function of n' and of Δn , and an advance on the theoretical side is due to Lenz†.

If the equilibrium is of a thermal type, then the distribution of energy among the initial states should be proportional to $e^{-\frac{E_n}{kT}}$, if E_n is the energy associated with vibrational

quantum number n . It has then been customary to describe the type of energy distribution in a spectrum as a low temperature or a high temperature distribution according as the intensity "gradient"—as n' increases outwards from (0, 0)—is in conformity with a small or large value of T . The Ångström band system—with $n'=0$ and 1 only—is, for example, typically a low-temperature distribution. On the other hand, the term "high-temperature distribution" is very wide, and covers such vastly differing cases as the violet CN bands and extreme cases like the ultra-violet oxygen bands, in which the possibility of the distribution being thermal in origin at all is quite ruled out.

In the case of the β -group above, it is clear that we cannot describe the energy-distribution among n' values as characteristic of either "high" or "low" temperature. If the columns from $n''=7$ to 10 were alone present we might say it was "low," but for very small and very large values it is decidedly "high" temperature.

We wish, however, to draw attention to a characteristic type of energy distribution which is found in a great many spectra. It is more common as a type of distribution among the final vibrational states (n'') than among the initial states, although it is found in both. Dealing now only with the distribution among the final states, Table III. indicates a typical high temperature non-thermal distribution for $n'=0$ (using these terms for the sake of convenience). For $n'=1$ there is a characteristic "instability" of the final states which in $n'=0$ were the most probable. This is still more notable for $n'=2$ and 3, and the effect seems to widen almost symmetrically, about $n''=9$ in the above case. Other

* *Loc. cit.*

† *Zeit. für Phys.* vol. xxv. p. 299 (1924).

such cases may be noted, *e. g.* the high-pressure CO bands*, which are a single n'' sequence. The (0, 1) band is the strongest, (0, 2) is almost absent, while (0, 3), (0, 4), etc., increase in intensity. The A and E systems of the CuI molecule† show the effect well. The SO₂ bands‡ also show the effect in a very striking manner. In the case of the third positive carbon bands we have found for the *initial* states that the sequence $n'=0$ is strong, $n'=1$ is faint, $n'=2$ and 3 are absent, and $n'=4$ is faint.

Returning to the β -system with this typical distribution of intensity among the n'' states, we have not found it possible as yet to suggest any adequate cause. It seems possible, however, that the emitting electron in this case is exceedingly sensitive to perturbation arising from vibrational motion of the nuclei, so that some distinct internal change (such as a change of *type* of the electronic orbit) takes place if one quantum of vibration is acquired. This configuration change, whatever it be, is exaggerated for molecules existing with two vibrational quanta, and so on. Some such cause may account for the difference in behaviour of the $n'=0$ sequence from the others, $n'=1, 2$, and 3; but the origin of the instability of a number of the n'' states is very obscure, particularly as the n'' level of the β -system is the normal level. If there were a system in the infra-red having its final level in common with that of the β -group (*i. e.* the normal level), then the overlapping of the very extensive final vibrational levels of the β -group with the initial vibrational levels of this hypothetical system might account for the facts. This, however, seems unlikely for two reasons:

- (1) The hypothetical system would need to extend into the visible region to account for the observed range of instability.
- (2) Such an explanation is unlikely to hold generally, and the observed phenomenon is characteristic of a *class* of molecules.

It is perhaps worth noting that in the $n'=3$ sequence of the β -group (see Table III.) there is evidence of *two* minima in the intensity distribution among the n'' values.

The factors governing the distribution of energy among the vibrational states of a molecule provide a very big field of investigation both for the theorist and the experimental spectroscopist.

February 6th, 1926.

* Proc. Roy. Soc. A, vol. ciii. (1923), plate.

† Phys. Rev. vol. xxvi. diagram, p. 20 (1925).

‡ Proc. Roy. Soc. A, vol. cvi. p. 215 (1924), plate.

LVI. *On the Arc Spectrum of Lead.* By NALINI KANTA SUR, M.Sc., University of Allahabad*.

1. INTRODUCTION.

KAYSER and Runge † were the first to note regularities in the arc spectrum of lead. Their results were extended by Saunders ‡, Zumstein §, and Meissner ||, but the first important step towards the classification of the spectrum into series was taken by Thorsen ¶, who studied the arc spectrum of lead with quartz spectrographs of high dispersion, and was thus able to measure the wave-lengths of many weak lines not recorded before. From these data Thorsen identified the sharp and diffuse series characteristic of a triplet system, and found that the limits $2p_1$, $2p_2$, and $2p_3$ of these series had the separations 10810·8 and 2831·8 respectively, as found by Kayser and Runge.

The absorption spectrum of lead vapour was first studied by McLennan and Zumstein **, and later on reinvestigated by Grotrian ††, and independently by Sur and Sharma ‡‡, up to a temperature of 1300° C. Grotrian, as a result of his absorption experiments at different temperatures, introduced another term $2p_4$ corresponding to the normal state of the atom. According to him the line $\lambda=2833\cdot17 \text{ \AA.}$, which is the first line to come out in absorption and which was not included in Thorsen's scheme, is produced by the combination of $2p_4$ with $2s$. This extension of Thorsen's scheme leads to the conclusion that $\lambda=2170\cdot07 \text{ \AA.}$, and $\lambda=2053\cdot83 \text{ \AA.}$, which satisfy the combinations $2p_2-3d_2$ and $2p_4-3s$ respectively, should also be absorbed simultaneously with $\lambda=2833\cdot17$ at the same temperature. Grotrian was unable to obtain these lines in absorption, but the simultaneous absorption of $\lambda=2833\cdot17 \text{ \AA.}$ and $\lambda=2170\cdot07 \text{ \AA.}$ at the same temperature was noted independently by Sur and Sharma §§, who, as well as Grotrian, were unaware of the

* Communicated by Prof. M. N. Saha, D.Sc., F.I.P.

† Kayser and Runge, *Handbuch der Spectroscopie*, Bd. ii. p. 574.

‡ Saunders, *Astrophys. Journ.* xliii. p. 240 (1916).

§ Zumstein, *Trans. Roy. Soc. Canada*, Sec. iii. 59 (1918).

|| Meissner, *Ann. der Phys.* lxxi. p. 135 (1923).

¶ Thorsen, *Naturwissenschaften*, xi. p. 78 (1923).

** McLennan and Zumstein, *Trans. Roy. Soc. Canada*, Sec. iii. 9 (1920).

†† Grotrian, *Zeits. f. Phys.* xviii. p. 169 (1923).

‡‡ Sur and Sharma, *Journ. of the Science Association, Marahajah's College, Vizianagram*, J. 1, No. 4, pp. 121-124 (1924). Also *Science Abstracts*, xxviii. p. 43 (1925) (Abstract No. 126).

§§ Sur and Sharma, *loc. cit.*

work of McLennan and Zumstein*, who had previously found that the lines $\lambda=2170\cdot07$ Å., $\lambda=2053\cdot83$ Å., $\lambda=2833\cdot17$ Å. and $\lambda=2022\cdot64$ Å. were absorbed by normal lead vapour at a temperature of 750° C. Two other combination lines, $\lambda=1868\cdot7$ Å., $\nu=2p_4-4s$, and $\lambda=1904\cdot9$ Å., $\nu=2p_4-4d_1$, previously observed by Saunders†, justified the existence of the $2p_4$ term, and McLennan, Young, and McLay‡, as a result of their investigation of the lead arc-spectrum with a fluorite spectrograph, have made important verifications of the Thorsen-Grotrian Scheme by identifying nineteen more combinations.

To account for the absorption of $\lambda=3683\cdot47$ Å. at a temperature of 1000° C., the $2p_5$ term was introduced by Grotrian. The combinations with $2p_5$ are very few in number, and Zumstein§ concludes, from a later absorption experiment at high temperatures, that it is unnecessary to introduce the $2p_5$ term, and that $\lambda=3683\cdot47$ Å. is the first line of a series designated by him as the $2p_3-mx$ series, the separation between $2s$ and $2x$ being 327, as noted by Saunders|| and Meissner¶. In the same work, Zumstein suggests that $\lambda=10650\cdot8$ and $\lambda=6011\cdot76$ may be $2s-3p_2$ and $2s-4p_2$ combinations respectively, and, further, $\lambda=10291\cdot3$ Å. and $\lambda=5895\cdot68$ Å. may be the $2x-3p_2$ and $2x-4p_2$ combinations. If this is true, then higher members of these two series should be obtained in the region of spectrum $\lambda=6000$ Å.— $\lambda=4000$ Å. This suggested a reinvestigation of the arc lines of lead in that region, and many new lines of lead have been obtained as reported below.

But before passing on to the results of the present investigation, it is necessary to mention the important results obtained by Gieseler and Grotrian** in a recent work on the series classification of the arc-spectrum of lead, which came to hand during the course of the present work. These authors have excited the spectrum in the presence of a dense rain of electrons, after the method of Whiddington†† for exciting the higher members of the Balmer series of

* McLennan and Zumstein, *loc. cit.*

† Saunders, *loc. cit.*

‡ McLennan, Young, and McLay, Trans. Roy. Soc. Canada, Sec. iii. xviii. p. 77 (1924).

§ Zumstein, Phys. Rev. xxvi. p. 189 (1925).

|| Saunders, *loc. cit.*

¶ Meissner, *loc. cit.*

** Gieseler and Grotrian, *Zeits. f. Phys.* xxxiv. p. 374 (1925).

†† Whiddington, Phil. Mag. xlv. p. 605 (1923).

hydrogen, and have thus obtained some higher members of the series previously classified by Thorsen and by Grotrian himself, and also many new lines not recorded by previous observers. As they have recorded their results in terms of the new notation given by Sponer*, the relation between the new and old systems of notation is shown in the following scheme. From the different combinations Sponer has fixed the inner quantum numbers of the various terms, and following Sommerfeld has named them accordingly. Thus:—

Thorsen-Grotrian...	p_4	p_3	p_2	p_1	$3d_1$	$3d_2$	$3d_3$	$4d_3$.
Sponer	p_0	p_1	p_2	P_2	$3d_3$	$3d_1$	D_2	D_2 .
Gieseler-Grotrian ..	p_0	p_1	p_2	P_2	$3d_3$	$3d_1$	$3d_2$	$4d_3$.

In the new system, the suffixes denote the inner quantum numbers of the different terms. As shown in the above scheme, Sponer assigns the inner quantum number 2 to both the $3d_3$ and $4d_3$ terms, but Gieseler and Grotrian, for reasons mentioned in their paper, call it $3d_2$ and $4d_3$ terms respectively. Adopting this notation, Gieseler and Grotrian have shown that three higher members of each of the series P_2-ms , p_2-md , and P_2-md_1 , one member of each of the series p_2-md_2 , P_2-md_3 , and p_2-md_3 series, and two members of the series P_2-md_3 are obtained from the new lines recorded by them. They have been further able to identify the series p_2-mf_3 , P_2-mf_3 , P_0-ms , and P_0-md , and have thus definitely established the existence of a fifth P term, as is to be expected from the theoretical work of Pauli † and Heisenberg ‡, Goudsmit §, and Hund ||.

2. EXPERIMENTAL METHOD.

The arc-spectrum of lead was excited by the method of Hemsalech and de Gramont ¶. The positive pole was a thick copper plate, about 10 by 5 cm. in area, with a small depression in it to contain the molten lead. For the negative pole a rod of Acheson graphite was used, so that the impurities in ordinary carbon were avoided to a very large extent. A current of about 25 amperes was sufficient to produce a dense vapour of lead in the arc, the spectrum being photographed in the first order spectrum of a 5-foot

* Sponer, *Zeits. f. Phys.* xxxii. p. 19 (1925).

† W. Pauli, Jr., *Zeits. f. Phys.* xxxi. p. 765 (1925)

‡ Heisenberg, *Zeits. f. Phys.* xxxii. p. 841 (1925).

§ Goudsmit, *Zeits. f. Phys.* xxxii. p. 794 (1925).

|| Hund, *Zeits. f. Phys.* xxxiii. p. 345 (1925).

¶ Hemsalech and de Gramont, *Phil. Mag.* xliii. p. 291 (1922).

concave grating, with a dispersion of $11.12 \text{ \AA. per mm.}$ Photographs were taken on Lumière S.E. orthochromatic plates, these being specially sensitive to green and yellow regions of spectrum, and exposures of at least twenty minutes were necessary to record the faint lines. Six plates were measured with a Hilger comparator, and the wave-lengths were interpolated in the usual manner, with reference to standard lines of iron. Unfortunately, the wave-lengths are not as accurate as desired, as the average error could not be reduced below $.05 \text{ \AA.}$, and in the case of very faint lines, designated with intensity 0, the error is about $.08 \text{ \AA.}$ The existing tables of the wave-lengths for bismuth, zinc, cadmium, silver, copper, tin, silicon, aluminium, arsenic, sodium, potassium, phosphorus, and antimony were compared to eliminate the lines due to possible impurities, as chemically pure lead was not available. The wave-lengths of the lines measured are given in Table I.,

TABLE I.

I.Å.	Int.	Wave-number.	Remarks.
5818.56	1	17181.6	
5750.99	0	17383.5	
5743.47	0	17406.3	
5738.40	0	17421.6	
5727.03	4	17456.3	
5703.52	3	17528.2	
5692.20	8	17563.0	Walters (5692.26), Eder and Valenta.
5670.81	2	17629.3	
5608.87	8	17824.0	Walters (5608.85), Eder and Valenta.
5603.40	4 h	17841.4	
5598.76	4	17856.2	Cd ?
5594.20	5	17870.7	
5588.68	6	17988.4	
5534.74	3	18062.7	
5513.53	3 h	18132.2	
5459.3	0 h	18312	
5407.1	0 h	18489	
5372.5	0 h	18608	
5256.9	0	19017	
5241.48	1	19073.3	
5224.25	5	19136.2	Sn ?
5210.26	2	19187.6	Recorded in Kayser's <i>Handbuch der Spectroscopic</i> , vol. vi.
5206.34	1	19202.0	
5201.47	10	19219.9	Recorded in Kayser's <i>Handbuch der Spectroscopic</i> , vol. vi.
5173.01	3	19325.7	
5164.84	1 h	19356.3	
5163.67	1	19361.8	G.
5116.93	0	19537.5	
5108.62	4	19569.3	G.

TABLE I. (*continued*).

L.A.	Int.	Wave-number.	Remarks.
5090·65	8	19638·4	G.
5086·73	0	19653·5	
5077·35	1	19689·8	G.
5064·02	4	19741·7	
5043·57	1	19821·7	Obtained by Gieseler and Grotrian only.
5035·65	4	19852·9	
5024·43	3	19897·3	
5019·34	1	19917·4	
5005·45	10	19972·7	Recorded in Kayser's list.
4999·36	4	19997·0	
4981·30	6	20069·5	G, but measured as 4980·96.
4962·21	2	20146·7	
4900·21	2	20401·6	
4885·00	3	20465·1	
4875·71	4	20508·3	
4870·31	2	20526·9	
4864·95	3	20549·5	
4851·15	2	20607·9	
4831·66	2	20691·1	
4826·98	2	20711·1	
4820·25	1	20740·0	
4810·71	1	20781·2	Obtained by Gieseler and Grotrian only.
4723·68	3	21164·0	G.
4720·17	2	21179·8	G.
4718·59	1	21186·9	G.
4685·23	0	21337·7	Obtained by Gieseler and Grotrian only.
4680·62	0	21358·7	Obtained by Gieseler and Grotrian only.
4676·68	0	21376·7	Obtained by Gieseler and Grotrian only.
4664·86	3	21430·6	Obtained by Gieseler and Grotrian only.
4664·66	3	21514·7	G.
4618·21	2	21647·4	G.
4607·77	1	21696·4	Obtained by Gieseler and Grotrian only.
4602·52	4	21721·2	G.

"h" denotes that the line is hazy.

and it is rather surprising that so many new lines could escape the notice of the previous observers; but it may be mentioned here that Thorsen, McLennan and his co-workers, Gieseler and Grotrian, have also obtained many lines not previously recorded, and it seems that the arc-spectrum of lead still requires investigation in certain regions, which is being carried on.

3. RESULTS.

The lines of the arc-spectrum of lead, measured within the range of the spectrum $\lambda=4600-\lambda=5800$ Å., are noted in Table I. Reference is given to the lines, either previously recorded or recently by Gieseler and Grotrian,

in the column under remarks. The lines marked "G" denote that they have been recorded and measured by these observers also. The intensities were visually estimated, and are only true locally. Table II. contains all the pairs of

TABLE II.

	λ I.A.	Int.	Wave-number (vac.).	Diff.	λ I.A.	Int.	Wave-number.
1	13101.9	40	7630.5	326.7	12563.8	40	7957.2
2	10650.8	60	9386.4	327.9	10291.3	100	9714.3
3	6235.41	4	16032.3	328.3	6110.70	3	16360.6
4	6011.98	5	16629.5	327.4	5895.70	6	16956.9
5	5703.52	3	17528.2	328.0	5598.76	4	17856.2 cd?
6	5173.01	3	19325.7	327.8	5086.73	0	19653.5
7	5163.67	1	19361.8	328.0	5077.35	1	19689.8
8	5108.52	4	19569.7	327.6	5024.43	3	19897.3
9	5064.02	4	19741.7	327.8	4981.30	6	20069.6
10	4718.59	1	21186.9	327.8	4646.66	3	21514.7
11	4602.52	4	21721.2	328.6	4533.92	2	22049.8
12	4582.9	0 ^u	21814	328.2	4515.01	3	22142.2
13	2686.68	1	37209.6	328.5	2663.19	3	37538.8
14	2658.94	1	37597.8	327.2	2636.00	1	37925.0
15	2660.91	3	37570.0	329.3	2637.39	4	37899.3
16	2066.43	0	48377.1	328.3	2052.50	0	48705.4

Obtained
from Gieseler
and Grot-
rian's data
of new
wave-lengths.

lines having a separation of 328. These pairs have been tabulated from the data of the present writer, of Gieseler and Grotrian, and of previous observers. The first two pairs of wave-lengths of Table II. are noted in Rowland units, and have not been converted to international units, as the error in measurement exceeds the magnitude of the correction involved.

From Table II., it will be seen that there are four pairs of wave-lengths, with a separation of 328, which very approximately follow a Rydberg sequence. These are shown in Table III.

TABLE III.

$$2s = 24536 \quad 2x = 24864.$$

<i>m.</i>	$2s - mp_2$.	$2x - mp_2$.	mp_2 (observed).
			$2p_2 = 49173$
3.....	$\lambda = 10650.8 (60)$ $\nu = 9386.4$	$\lambda = 10291.3 (100)$ $\nu = 9714.3$	15149.6
4.....	6011.98 (5) 16629.5	5895.70 (6) 16956.9	7906.5
5.....	5108.52 (4) 19569.7	5024.53 (3) 19896.8	4966.3
6.....	4718.58 (1) 21186.9	4646.66 (3) 21514.7	3349.1

The observed value of the limit $2s$ is obtained from the combinations $2p_0 - 2s$, $2p_1 - 2s$, $2p_2 - 2s$, $2P_2 - 2s$, the values of the terms $2p_0$, $2p_1$, $2p_2$, $2P_2$ being 59821, 52004, 49173, 38365 respectively. These values are taken from Gieseler and Grotrian's paper, as they have been able to calculate more accurately the limits by exciting and measuring the wave-lengths of the higher members of the different series. The value of the term $2s$ as calculated by Gieseler and Grotrian is 23300, whereas the approximate value of the limit $2s$ calculated from the last two lines of the series $2s - mp_2$ is 24599, which closely agrees with the observed value 24536. The formula calculated from the last three lines of the series $2s - mp_2$ is

$$\nu = 24703 - \frac{N}{\left\{ m + 430251 + \frac{.766215}{m} \right\}^2 (m=3, 4, 5)}.$$

The correcting term is unusually large, so that the series does not closely follow a Rydberg formula.

From Table II., it can be further seen that there are three more pairs of wave-lengths with a separation of 328, which also closely follow a Rydberg sequence. These are shown in Table IV.

TABLE IV.

$$2s=24536 ; 2x=24864.$$

$m.$	$2s - mp_1.$	$2x - mp_1.$	$mp_1.$
3.....	$\lambda=13101.9$ (40) $\nu=7630.45$	12563.8 (40) 7957.2	$2p_1=5200.4$ $3p_1=16905.5$
4.....	6235.44 (4) 16032.3	6110.70 (3) 16360.6	$4p_1=8503.7$
5.....	5173.01 (3) 19325.7	5086.73 (0) 19653.5	$5p_1=5210$

The approximate value of the term $2s$ as calculated from the last two lines of $2s - mp_1$ and Rydberg's table is 24522. The calculated values 24599 and 24522 are in close agreement with the observed value 24536. The higher members of the series $2s - mp_1$ and $2x - mp_1$ have not yet been obtained, and one can only be sure about the correctness of the allocation of the lines to the series when they are discovered.

It will be noted that the third member of the series $2x - mp_1$ $\lambda=5086.73$ (I.A.) is very faint. It may be mentioned in this connexion that Gieseler and Grotrian * have recorded some anomalies in the intensities of the lines of some of the series of the arc-spectrum of lead. For example, the line $\lambda=5201.467$ (3) (I.A.) $P_0 - 3s$ is distinctly weaker than the line $\lambda=4157.826$ (5) (I.A.) $P_0 - 4s$. Some other irregularities in the intensities of the lines have also been mentioned by them.

There are two interesting inter-combination lines which have not been noted previously. The line $\lambda=7330.12$ (2) (I.A.), $\nu=13638.59$ is the combination $2p_1 - 2P_2$ ($5200.4 - 3836.5 = 1363.9$), and the new line $\lambda=4618.21$ (2) (I.A.), $\nu=21647.4$, recorded both by Gieseler and Grotrian and the present writer, is the combination $2p_1 - 2P_0$ ($5200.4 - 3035.5 = 2164.9$). The difference between the observed and calculated wave-numbers in the latter case does not exceed the uncertainty in the value of the limit $2P_0$, as calculated by Gieseler and Grotrian from the new series $P_0 - ms$ and $P_0 - md_1$, identified by them.

* Grotrian and Gieseler, *loc. cit.* p. 386.

From the new lines recorded and measured by Gieseler and Grotrian in the ultra-violet region, we also find four pairs of wave-lengths with a separation of 10806·6 as follows :—

	λ (I.A.).	Int.	ν .	$\Delta\nu$.	λ (I.A.).	Int.	ν .
1	2052·50	(0)	48705·4	10806·1	2637·79	(4)	37899·3
			$\Delta\nu=328\cdot3$				$\Delta\nu=329\cdot3$
2	2066·43	(0)	48377·1	10807·1	2660·91	(3)	37570·0
3	2060·52	(2)	48515·8	10806·1	2651·07	(4)	37709·4
4	2061·82	(1)	48485·3	10806·8	2653·24	(5)	37678·5

According to Gieseler and Grotrian, the separation between the values of the calculated limits $2p_2=49173$ and $2P_2=38365$ is 10808 ; hence the above lines can be represented as

$$\left. \begin{matrix} 2p_2 \\ 2P_2 \end{matrix} \right\} -467\cdot6, \quad \left. \begin{matrix} 2p_2 \\ 2P_2 \end{matrix} \right\} -795,$$

$$\left. \begin{matrix} 2p_2 \\ 2P_2 \end{matrix} \right\} -657\cdot5, \text{ and } \left. \begin{matrix} 2p_2 \\ 2P_2 \end{matrix} \right\} -687\cdot5$$

Now the second terms have very small values. The lines can therefore be either some higher members of some series, or may form a negative sequence analogous to the lines, discovered by Russell and Saunders * in the arc-spectrum of calcium. The first alternative does not fit in the scheme for the known series converging to either $2p_2$ or $2P_2$, and to test the second, further data are necessary, the region of the spectrum in which the expected lines are to be found being not yet explored.

It will also be noted that the separation 328 occurs in the first two pairs of lines of the above scheme. As it has not been yet possible to ascertain either the nature of the $2x$ term, or the significance of the separation $2s-2x$ occurring in other pairs of lines noted in Table II., it is difficult to decide whether this agreement of separation is real or accidental.

Finally, it may be mentioned that according to the scheme of the constitution of the arc-spectrum of the elements, carbon, silicon, germanium, tin, and lead of the fourth group of the periodic table, as discussed by Hund †, one of the five p -terms as given in the Thorsen-Grotrian scheme may be a D-term, and the other may be a S-term belonging to the

* Russell and Saunders, *Astrophys. Journ.* lxi. p. 38 (1925).

† Hund, *Zeits. f. Phys.* xxxiv. p. 301 (1925).

singlet system. If we identify the P_2 term with $^1D_2$ term and P_0 term with $^1S_0$ term (Notation of Russell and Saunders), then the lines $\lambda=7330.12$ and $\lambda=4618.21$ correspond to the inter-combinations $^3p_1-^1D_2$ and $^3p_1-^1S_0$ respectively; but there are other difficulties in reconciling this assumption with the relations which are already known to exist.

SUMMARY.

With a view to obtaining the higher members of the Rydberg sequence in the series spectrum of lead, the spectrum has been reinvestigated, using the heavy-arc method of Hemsalech and de Gramont. Several members of the series $2s-mp_{1,2}$ and $2x-mp_{1,2}$ have been obtained. Indications have been obtained that the arc-spectrum of lead contains negative terms, similar to those discovered by Russell and Saunders in the arc-spectrum of calcium, and ascribed by them to the simultaneous excitation of the two outer electrons. Two combination lines between the principal terms have been obtained.

In conclusion I wish to record my best thanks to Prof. M. N. Saha for his guidance and interest in the work.

March 3, 1926.

LVII. *Scattered X-Rays. The J Phenomenon* (Part IV.).
By Prof. C. G. BARKLA, F.R.S., and Dr. S. R. KHASTGIR,
University of Edinburgh *.

INTRODUCTION.

IN a previous paper † we showed that when a heterogeneous X-radiation was scattered, the primary and scattered radiations had either $\begin{cases} (1) \text{ exactly equal absorbability, or} \\ (2) \text{ markedly different absorbability,} \end{cases}$ when measured in any particular substance. The one was an unmodified, the other a modified scattered radiation. In these results we found no support whatever for Compton's theory of quantum scattering. In every feature the difference observed between the primary and scattered radiations, when it appeared, was found to be due to what we have called the

* Communicated by the Authors.

† "The J Phenomenon in X-Rays.—Part II. Application to Scattered X-Rays," *Phil. Mag.* November 1925. See also Barkla and Mackenzie, "Notes on the Superposition of X-Rays and on Scattering. The J Phenomenon (Part III.)," *Phil. Mag.* Feb. 1926, and 'Nature,' Feb. 13, 1926.

J phenomenon. We showed, and we now propose to show more completely, that the difference observed depends upon the material used to test the radiation, *i. e.* upon the material used to compare the primary and secondary radiations.

Thus the difference between the scattered radiation and the primary as observed by us, is not a difference of wave-length as generally understood. It is a difference in the properties of the two radiations such as we are quite familiar with not only between a primary and scattered radiation, but under certain conditions between (a) two primary beams proceeding from the same source in different directions; (b) between two scattered radiations proceeding from the same source in slightly different directions; (c) it is a difference such as under suitable conditions occurs between either a primary or scattered radiation, and the same radiation subsequent to the slightest amount of filtering; (d) it is a difference such as appears under suitable conditions in a beam when a very feeble radiation is added to it *. These are not differences in the length of waves, and though the difference we have observed (when it appears) is of the magnitude to be expected on Compton's theory for wave-lengths in the neighbourhood of that of Mo 'K' radiation, this agreement is not general. In fact, beyond this chance agreement a comparison of our experimental results with Compton's is rather a comparison of contrasts. It is natural then to suggest that the occurrence of the J phenomenon in the scattered radiation is quite distinct from Compton's change of wave-length on re-emission (so-called scattering). But different though the Compton effect and the J-transformation are, both in the laws governing them and in the principles apparently underlying them, there is a correspondence between them which is too remarkable to admit of their independence. In addition, apart from the J-transformation of the scattered radiation, no evidence of the Compton change of wave-length appears in our experiments; it is simply not there. It should be remembered, however, that (1) we have experimented upon the scattering of heterogeneous beams, and (2) we have measured absorbability of radiations instead of an angle of diffraction, *i. e.* an angle at which tertiary rays appear from a crystal. The advantages of our method have already been stated.

This paper is principally concerned with three points:—
(1) We show quite definitely that while the secondary differs

* (e) and it is possibly, though not so certainly, a difference such as occurs between two characteristic radiations from the same substance under slightly different conditions.

from the primary radiation when its absorbability is examined in certain substances, it is precisely like the primary when its absorbability is measured in other substances. In other words, what to some substances is a modified scattered radiation is to others an unmodified radiation.

It was indeed shown in a previous paper that a difference between primary and secondary radiations appeared over very limited ranges of wave-lengths when measured in one substance, while there was no difference when measured in another substance. This, however, is more convincingly shown by the experiment described below. This cannot be reconciled with a change of wave-length on scattering, for that might be expected to be shown by absorption in *all* substances.

(2) This seemed to suggest the possibility of a change of wave-length occurring in the scattered radiation, not in the process by which it originated, but later when passing through the testing substance which exhibits the difference of absorbability. We therefore pursued the matter further and found that even after a difference between secondary and primary had been demonstrated in one substance, there was no difference between primary and secondary when tested by certain substances placed behind the first. That is, although the second substance *may* show the difference between primary and secondary radiations, it does not do so necessarily, for each testing substance has its own critical condition. We are therefore justified in saying that there is in our experiments no evidence of change in wave-length either in the process of re-emission or in the subsequent transmission through matter.

(3) Further, we have found no gradual variation of absorbability of a scattered radiation with the angle of scattering such as Compton's theory indicates. Frequently, no difference appeared between two radiations scattered at different angles. Where, however, a difference did appear, while it was in the right direction, it was the very precise difference which characterizes a "J discontinuity"; it was the familiar step between radiations on two sides of such a discontinuity; it was the difference between two well-defined absorption levels.

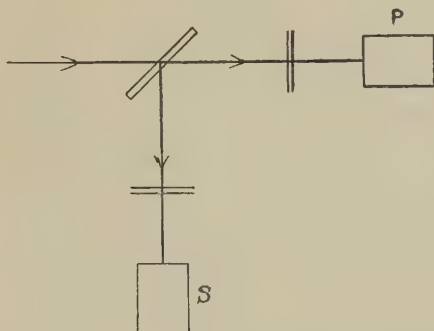
EXPERIMENTS.

Dependence on Testing Substance.

The ratio of the ionizations produced in two similar electroscopes by the secondary and primary beams was observed, first when the beams were unintercepted and

subsequently when intercepted by similar sheets of any particular substance (fig. 1). As previously indicated, the "intercepted ratio" S'/P' is frequently less than the "unintercepted ratio" S/P , because of the greater absorbability of the secondary beam; and as the thickness of the absorbing sheets is increased the ratio S'/P' falls. Plotting S'/P' against the thickness of absorbing substance, we thus get a curve sloping down to the right. A horizontal line would indicate equal absorption of secondary and primary radiations. Such a line is frequently obtained*; it indicates unmodified scattering. Now observe the results obtained and indicated in fig. 2 and Table I.. when the absorbing substances were aluminium, copper, silver, tin. It should be noticed that equal distances along the horizontal axis represent approximately equivalent thicknesses of the various absorbing

Fig. 1.



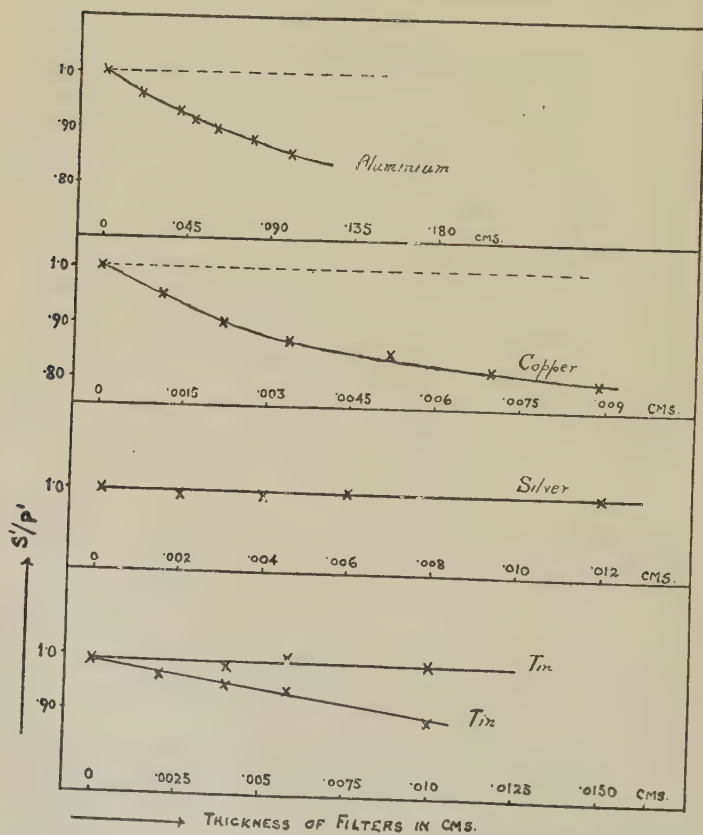
substances for a 50 per cent. absorption of the original unfiltered beam, *i. e.* .045 cm. of Al, .0015 cm. of Cu, .002 cm. of Ag, and .0025 cm. of Sn were approximately equivalent in absorbing power, as measured by a short air electroscope. Observing the two upper curves, it will be seen that aluminium and copper indicated quite consistently that the secondary (scattered) radiation was more absorbable than the primary— S'/P' steadily diminished by transmission, and by the same amount in the two substances. They thus gave consistent results indicating a modified scattered radiation. But from the third line it is seen that when measured in silver the secondary and primary radiations were identical: they were cut down to exactly the same extent by equal absorbing sheets, and the ratio S'/P' remained constant and equal to S/P . Thus in aluminium and

* Illustrated in previous papers.

646 Prof. C. G. Barkla and Dr. S. R. Khastgir on the copper the difference between secondary and primary was shown very markedly; in silver it did not appear at all.

Fig. 2.

Showing that what to Al and Cu is a modified scattered radiation is to Ag an unmodified radiation, and to Sn is sometimes one, sometimes the other.



Further, when tin was used the difference between secondary and primary appeared in some observations but not in others; and the various observations showed either no difference between secondary and primary or the well-marked difference*. The difference when it appeared was approximately half that shown by aluminium and copper.

* Bracketed numbers in Table I. show the order in which observations were taken.

TABLE I.

Absorbing substance.	Thickness of Absorbers.	Observed ratio $\frac{\text{Secondary}}{\text{Primary}}$ (arbitrary units).
Aluminium.	0.0 cm.	1.00 $\times x$
	.02 "	.96 "
	.04 "	.93 "
	.048 "	.91 (5) "
	.06 "	.90 "
	.08 "	.88 "
	.10 "	.85 (5) "
Copper.	0.0 cm.	1.00 $\times x$
	.0011 "	.95 "
	.0022 "	.90 "
	.0034 "	.87 "
	.0052 "	.85 "
	.0070 "	.82 "
	.0089 "	.80 "
Silver.	0.0 cm.	1.00 $\times x$
	.002 "	.99 "
	.004 "	.99 "
	.006 "	1.00 "
	.012 "	.99 (5) "
Tin.	(1) 0.0 cm.	1.00 $\times x$
	(3) .002 "	.98 "
	(9) .002 "	.97 "
	(4) .004 "	.99 "
	(5) .004 "	.96 "
	(8) .0058 "	1.00 "
	(6) .0058 "	.95 "
	(2) .01 "	.89 "
	(7) .01 "	1.00 "

Thus when measured in silver and in some cases when measured in tin, the absorption of the scattered radiation was identical with that of the primary. This may be called unmodified scattering. But the same unmodified scattered radiation appeared as a modified scattered radiation when measured in paper, aluminium or copper, and modified to a smaller extent) when measured in tin and gold. Again, a natural criticism of the experimental results if they were of doubtful accuracy, might be that silver and tin are not so sensitive to a change of wave-length of a more or less heterogeneous beam because their K characteristic radiations have a wave-length within the range of these experiments, and thus the diminution of the L, M, N absorptions with

increase of frequency might be roughly compensated by the appearance of the K absorption. A sufficient answer to that is that silver and tin *do show* the difference between primary and secondary when the critical condition is obtained in these substances, *i. e.* when a J-discontinuity in silver or tin is produced. It is perhaps unnecessary to show the results of such experiments; the truth is sufficiently clear for tin in fig. 2, though other experiments illustrate it with greater accuracy.

As the scattered radiation differs from the primary when measured in some substances, and not when measured in others, the question naturally arises, do substances of the former class when used to measure the absorbability *produce* the change—say of wave-length—in the secondary radiation and subsequently show that change? It appeared that such a transformation might possibly take place, for the J-discontinuity involving a change of absorption coefficient has been shown to be produced by mere filtering of a heterogeneous radiation. The answer to this question can be given if we can find any one substance which shows no difference between these scattered and primary radiations *subsequent* to these having been proved different when measured in other substances. In fig. 3 curves are shown giving the relation between S'/P' and thickness of absorbing substance, firstly when that absorbing substance was alone, and secondly when accompanied by a sheet of a second absorbing substance which did not show the difference between primary and secondary.

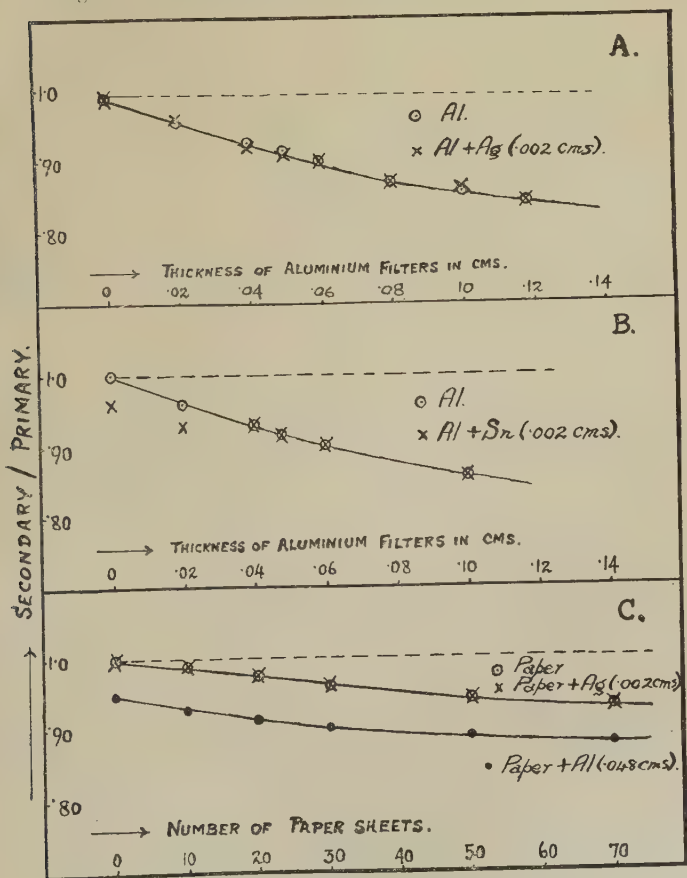
Thus, curve A shows by circles the value of S'/P' for various thicknesses of intercepting aluminium. The slope shows the intensity of the secondary to fall more rapidly than the primary. But when, in addition to the aluminium, sheets of silver (.002 cm. thick) were placed in both beams, the ratio S'/P' was absolutely unchanged, as shown by the crosses. Transmission through silver produced no further change in the ratio of the secondary to primary,—that is they were equally absorbable in silver.

Curve B was obtained in precisely the same manner, but tin was used as the second absorbing substance. In this case the tin sheet definitely did absorb the scattered radiation more than the primary in two cases, as is shown by the two crosses below the circles. But in the other cases transmission through tin produced absolutely no change in the ratio of secondary to primary: crosses and circles are superposed. Thus, in agreement with previous experiments, tin showed the

difference in some experiments and not in others, though they were all in the same series.

Fig. 3.

Showing that after transmission through substances Al and Paper which indicate a "modified scattered radiation" this is still "unmodified" to Ag and sometimes to Sn.



Exper. A. Filtering by Al (○); Al with Ag .002 cm. (×).
 " B. " " (○); " Sn .002 cm. (×).
 " C. " " Paper (○); Paper with Ag .002 cm. (×).
 " " " Paper with Al .048 cm. (•).

(Curve C shows by circles the ratio S'/P' after transmission through paper of varying thickness; by crosses a similar ratio after passing through silver in addition to the paper; and by dots the corresponding ratios after transmission

through aluminium in addition to the paper. The results show that after transmission through paper, which shows the difference between scattered and primary, the difference is also shown in aluminium, but is not indicated to the slightest extent in silver. Yet silver is quite capable of showing a difference when certain conditions are attained, as is indeed shown above in the case of tin.

Thus a change of absorbability of X-radiation by scattering is dependent on a relation between the radiation and the substance used to test those radiations. There is absolutely no difference in the absorbability when tested in some substances—even subsequent to transmission through those substances which exhibit a difference. How then can there be a wave-length change either in scattering or in the subsequent transmission of the scattered radiation through matter? Can wave-length depend upon the testing substance, or can even the evidence of a change of wave-length be shown so markedly in some substances and not at all in others?

Scattering at Various Angles.

According to Compton's theory of quantum-scattering of X-rays the change of wave-length produced by scattering is given by $\delta\lambda = 0.24(1 - \cos \phi)$ Ångström units, and thus should vary with the angle of scattering ϕ . Again we have found no confirmation of this by the absorption method: what has been observed has been either absolutely no difference or a well-marked difference between the secondary radiations proceeding in two directions, and this difference is due to a definite step in the activity and absorbability such as is characteristic of the J phenomenon. Thus the variation with angle occurs only in steps, between which there is no variation at all.

Barkla and Miss Mackenzie* showed that when a difference between the two beams scattered at 60° and 120° with the direction of propagation of the primary did appear, it was in one of two forms (a) or (b). In case (a) the difference was not one of general absorbability, but was shown by sudden changes in the ionization produced by the beam at 120° when by absorption it reached certain absorbabilities, while the beam at 60° did not show these discontinuities. In case (b) the beam at 120° was continuously more absorbable than that at 60° . Case (a) obviously indicated no change of wave-length, for there was no difference in absorbability. Case (b) had the superficial appearance of a difference in wave length, but

* Phil. Mag. Feb. 1926.

other experiments showed that the difference of absorbability was the precise difference involved in the change of level of the activity called the J-transformation, and was due simply to a difference in the properties of the two radiations depending on something quite different from wave-length. This something is a property of the beam as a whole and not of its constituent wave-lengths, except as they contribute to some kind of average for the whole stream of radiation.

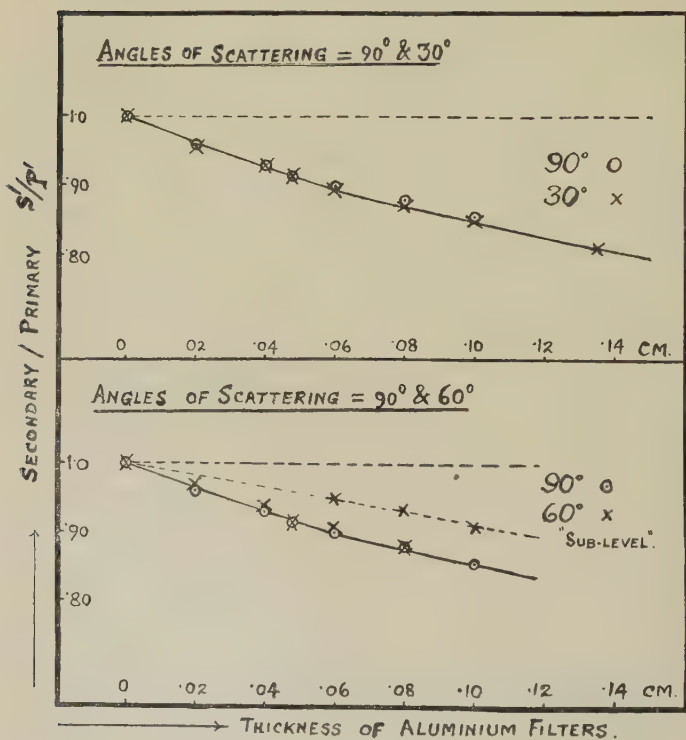
Instead of comparing the two scattered beams directly we have in these experiments compared the radiations scattered at various angles 30° , 60° , and 90° with the primary radiation producing them. This we did, as before, by placing equal thicknesses of absorbing aluminium in the path of both primary and secondary radiations. Briefly the results may be stated thus:—When the difference between the primary and secondary is observed, in general it has the same magnitude whatever the direction from which that secondary radiation proceeds, within the limits of J-discontinuities. Any variation with angle occurs in the familiar finite steps of the J-discontinuities. In the Barkla and Mackenzie experiments it was the scattered radiation at 120° which differed from the primary, while that at 60° was like the primary (or differed from it by a constant smaller amount).

Fig. 4 shows in its upper section the results of experiments by which the scattered radiations at 30° and 90° were compared with the primary radiation and with one another. As before, the ordinates are values of S'/P' for the various values of the thickness of aluminium intercepting both secondary and primary beams. The slope of the curve measures the difference between secondary and primary beams. The circles represent observations made upon the radiation scattered at 90° , while the crosses give the corresponding values for S'/P' when the scattered radiation experimented upon was at an angle of 30° . The almost perfect superposition of circles and crosses shows that while they both differed considerably from the primary, the two secondary beams had identical absorbabilities. In the lower section of fig. 4 a similar comparison is made between the radiations scattered at 60° and 90° . In this case again, the two scattered beams had identical absorbabilities in a number of measurements; whereas three other measurements showed the beam at 60° to be distinctly less absorbable than that at 90° . This change is of the kind that would be given by Compton's variation of wave-lengths with scattering angle.

It indicates, however, only a definite change of the level of activity of the radiation governed not by wave-length but by a quality of the whole radiation. The difference between the primary and scattered radiations is again shown for

Fig. 4.

Comparing radiations scattered at different angles.

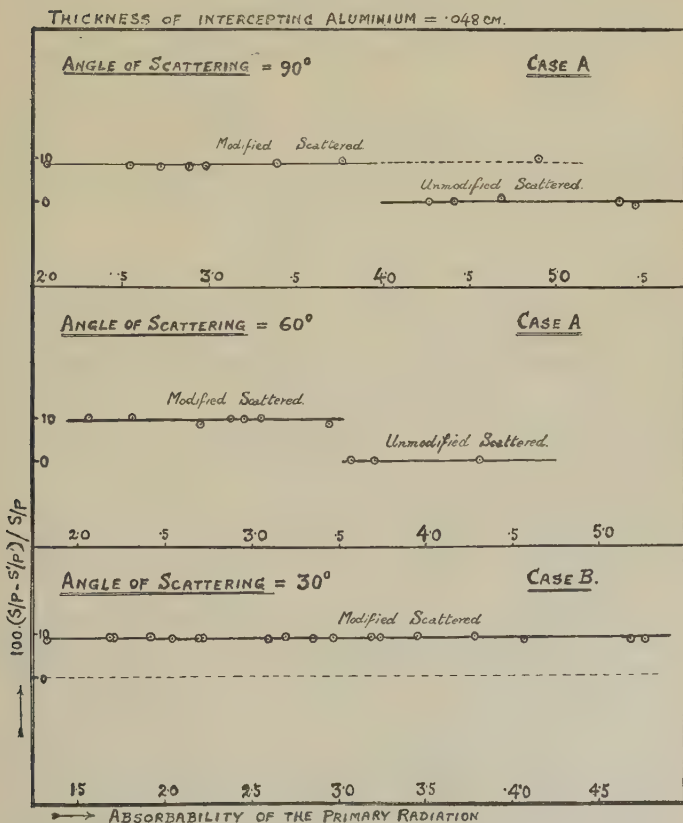


various angles of scattering in fig. 5. In this case the intercepting aluminium was of constant thickness while the wave-length of radiation varied. The difference is seen to be independent of the angle, *i. e.* the same for 30°, 60°, and 90°. The ordinates show the percentage change in the ratio S/P produced by transmission of both primary and secondary beams through .048 cm. of aluminium (S'/P'). It will be observed that for soft radiations (the right-hand side of the figure) there was absolutely no difference between secondary and primary beams scattered at 90° and 60°, but at the more

penetrating end the scattered radiation appeared markedly softer than the primary, the percentage change in the ratio S'/P' being about 9 per cent. *whatever the original absorptivity of the radiation and whatever the angle of scattering.* This corresponds to a constant difference of absorption coefficient between primary and scattered. [See previous paper.]

Fig. 5.

Showing the degree of "modification" to be independent of angle of scattering.



The difference between secondary and primary when it appeared at all was thus independent of the angle of scattering. (It would appear from the results shown in fig. 5 that when soft radiation was used the radiation scattered at 30° was more absorbable than that scattered at 60° and 90° .)

These experiments were, however, made at different times, consequently with different radiations. A direct comparison at the same time, *i. e.* with a given primary radiation, has never shown the radiation scattered at the smaller angle to be more absorbable than that scattered at greater angle). Again, the phenomenon is simply an illustration of the J-transformation, *i. e.* a change in the level of the activity due to characteristics of the radiation other than wave-length.

It should be noted that Compton's theory indicates a very minute change of wave-length by scattering at 30° ; for high frequencies at this angle our observed change in absorption is thirty times that calculated after Compton; whereas for low frequencies *when no modification was observed* at 90° it was less than $1/10$ (possibly $1/20$) of what would be expected on the Compton theory. As previously indicated, there is close agreement when a modification does appear for wave-lengths in the neighbourhood of that of "Mo K" radiation and the scattering angle is 90° . But the agreement is accidental.

SUMMARY OF EXPERIMENTAL RESULTS.

The following results, which were obtained and confirmed in many experiments, are illustrated in the preceding paper:—

(1) When a heterogeneous X-radiation is scattered, the scattered radiation has either precisely the same absorbability as the primary, or there is a well-marked difference between the absorbabilities when measured in any one substance. (Shown in previous paper.)

(2) When the scattered radiation is different from the primary when measured in certain substances, its absorbability may be, and frequently is, precisely like that of the primary when measured in certain other substances.

(3) Even after transmission through substances which show the difference between primary and secondary radiations, there is still no difference between the two when measured in certain other substances.

(4) When the scattered radiation is observed in different directions making angles of 30° , 60° , and 90° with the primary beam, and when these radiations differ from the primary in their absorbability in a certain substance, they, in general, differ by precisely the same amount. When a difference appears with increasing angle of scattering, it takes place abruptly—by a jump.

DISCUSSION.

The above facts are all explained in terms of the J phenomenon—that there are different possible levels for the

activity of a beam of X-rays, the particular level of activity being dependent not upon any constituent wave-length of the radiation, but upon a coherence of the whole radiation and upon the relation between the average constitution of the radiation (closely allied to temperature) and characteristic "temperatures" of the substance traversed.

Indeed, in all our investigations upon the scattered radiation, the difference which we have observed between it and the primary is a difference such as also appears through operations quite different from scattering. It is a difference due to properties of a coherent beam and may under suitable conditions be produced by slight filtering, or by the superposition of a feeble radiation upon the beam studied, or in other ways. *These* cannot be, or should not be, described as changes in wave-length.

On the other hand, we find absolutely no indication of Compton's wave-length change by scattering, and all the laws governing the change observed by us—the manner of its appearance, its magnitude, its variation with frequency and with the angle of scattering—appear entirely at variance with Compton's view.

All the apparent conflict of results may just possibly be due to the fact we have already established—that a considerable portion (at least) of the properties of an X-radiation is not fundamentally associated with the wave-length, but with this "temperature," measured to a certain degree of approximation by absorption-coefficient,—that Compton measures one property; we measure another, a more intimately related one; and that these two properties are not related in the way which experiments upon homogeneous radiations have indicated. But though a change in activity,—a change in properties,—is certainly brought about by methods which cannot involve a change in wave-length (but only a slight change of average wave-length or a change of "temperature" of the whole beam), the assumption that a change of wave-length of such magnitude as that of the Compton effect could occur without some corresponding marked change in the ionizing and penetrating properties of the radiation such as we could easily detect, is too revolutionary to accept without either experimental or theoretical justification. It would mean that the properties are practically independent of wave-length or frequency of the constituent radiations. Yet apart from that, there is no alternative to the conclusion that the Compton effect does not occur in our experiments on heterogeneous beams and without a diffracting crystal.

Besides that, in place of the Compton effect we observe the J-transformation, which though governed by different laws

shows a remarkable correspondence with the Compton effect. The alternatives thus are:—

- (1) No Compton effect in all our experiments, or
- (2) A complete divorce of the activity of an X-radiation from wave-length, and the substitution of an entirely new system of laws.

Briefly then, we find that the difference between a scattered and a primary X-radiation is simply expressed by saying that the scattered radiation has characteristics of structure which make it much more favourable to the J phenomenon than is the primary radiation. The fact of *coherence* suggests a reason for this, for coherence implies a certain persistence (a continuity of action) such as might be produced by

- (1) a scattered radiation when the primary radiation is too intermittent to cohere ;
- (2) a scattered radiation making a large angle with the primary when that making a small angle is not sufficiently homogeneous (on a large scale) ;
- (3) a scattered radiation from a thick radiator when that from a thin radiator is not sufficiently homogeneous.

The hypothesis would also explain the apparently capricious nature of the J phenomenon, for the stream of X-radiation might be expected to be sufficiently continuous (sufficiently homogeneous) by some methods of excitation and not by others. Such a dependence on the details of excitation has been found (Barkla and Mackenzie, unpublished).

This explanation is as yet merely hypothetical and should be distinguished from the *fact of coherence* of the constituent radiations in a beam. Of this there can be no possible doubt. Quite outside the sphere of speculation is the fact that the ionization produced by a beam of X-rays is not dependent on

- (1) simple wave-length and intensity on the one hand (classical theory),
- or (2) independent quanta and the number of these on the other hand (quantum theory),
- or (3) any combination of these ;

but, in part at least, upon a quality of the full stream of radiation more closely allied to temperature. This is the meaning of the J phenomenon, and this forms the basis of the explanation of all we have observed in our comparison of the scattered and the primary X-radiations.

The J phenomenon will be further described and discussed in later papers.

LVIII. *The Compton Effect and the Reflexion of X-Rays by Crystals.* By E. J. WILLIAMS, M.Sc., Fellow of the University of Wales*.

§ 1. *Introduction.*

IT has been found by A. H. Compton that when X-radiation is scattered by matter the wave-length of part of the scattered radiation is longer than that of the incident radiation, the rest of the scattered radiation being unmodified. The bearing of this phenomenon on the diffraction of X-rays by crystals has, so far, received little attention†. In calculating the positions and intensities of the diffracted beams, it has been assumed that all the radiation scattered by the electrons in the crystal has the same wave-length as the incident radiation. It is found that the laws of reflexion derived on this supposition are obeyed by *all* the radiation reflected by a crystal, from which it follows that either (1) no modified radiation is reflected by a crystal, or (2) the modified radiation obeys the same laws of reflexion as the unmodified radiation to within the error of observation. Should (1) be correct, it is possible that we must modify the estimates of the intensity of reflexion based on the assumption that the scattered radiation in every respect obeys the classical laws. For the total amount of radiation scattered, including modified and unmodified, corresponds to the amount given by the classical theory, so that, if the electrons in the crystal scatter modified radiation which is not reflected, only part of this amount will be available for building up diffraction maxima. It is the purpose of this paper to examine these questions, and in particular to investigate the effect on the intensity of reflexion. The laws of reflexion of the modified radiation will first be considered in order to test the possibility of (2).

§ 2. *Laws of Reflexion of Modified Radiation.*

In order to consider a phenomenon of interference it is necessary in the present state of radiation theory to assume the wave theory. Furthermore, in order that a change of wave-length be intelligible on the wave theory it is necessary to suppose the scattering electrons to be moving,

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† In a recently published paper (*Zeit. für Phys.* xxxvi. 2, 1926) Kellmann and Mark consider some aspects of the question, and reference will be made to their work in the parts concerned.

in which case a change in wave-length follows as a Doppler effect. A supposition of this nature was made by Compton * in considering the distribution and intensity of the modified radiation scattered by an amorphous substance. He showed that, if the scattering electrons travelled in the direction of the incident rays with a velocity $h/m\lambda$, the wave-length of the radiation scattered in any direction would be that required by the quantum theory of scattering. Compton showed that the calculated distribution obtained in this way is in substantial agreement with the observed distribution, and this result warrants the use of the same method in order to obtain the laws of reflexion of the modified radiation. The supposition made here is that the actual distribution of the diffracted beams is the same as that which, on the classical wave theory, would result from the scattering of the radiation by an electron lattice moving with the velocity $h/m\lambda$.

Let λ = wave-length of the incident X-radiation as measured by a stationary observer ;

ox = direction of incident rays, so that the moving scatterers have a velocity $h/m\lambda$ parallel to ox .

Then for an observer moving with the scatterers the wave-length of the radiation before and after scattering is $\lambda(1 + \beta)$ where $\beta = h/m\lambda c$, powers of β higher than the first being neglected. The angles of incidence and reflexion measured by this observer are given by Bragg's law, and we have

$$2d \sin \theta = n\lambda(1 + \beta), \quad . \quad . \quad . \quad . \quad (1)$$

where θ is the common value of the angles of incidence and reflexion.

As the direction of motion is parallel to the incident rays the angle of incidence is the same for the two observers. The angle of incidence, ϕ_i , measured by the stationary observer is therefore given by

$$2d \sin \phi_i = n\lambda(1 + \beta). \quad . \quad . \quad . \quad . \quad (2)$$

If ϕ_r denote the angle of reflexion, then $\phi_i + \phi_r$ is the angle between the reflected rays and the direction of relative motion measured by the stationary observer. The angle between the reflected rays and the direction of relative motion is 2θ for the moving observer, so that from the law of aberration †

$$\cos 2\theta = \cos(\phi_i + \phi_r) - \beta / 1 - \beta \cos(\phi_i + \phi_r). \quad . \quad (3)$$

* Phys. Rev. 2, xxi. (1923).

† Vide, e.g., O. W. Richardson, 'Electron Theory of Matter,' p. 306.

It follows from (1), (2), and (3), on neglecting higher powers of β , that

$$2d \sin \phi_r = n\lambda(1 - \beta + 2\beta \sin^2 \alpha), \quad \dots \quad (4)$$

α denoting the angle of reflexion of the unmodified radiation. On substituting for β its numerical value, (2) and (4) become respectively

$$\left. \begin{aligned} 2d \sin \phi_s &= n(\lambda + \cdot 024), \\ 2d \sin \phi_r &= n(\lambda - \cdot 024 + \cdot 048 \sin^2 \alpha), \end{aligned} \right\} \quad \dots \quad (5)$$

d and λ being expressed in Ångström units.

The common value, α , of the angles of incidence and reflexion of the unmodified radiation is given by

$$2d \sin \alpha = n\lambda. \quad \dots \quad (6)$$

The laws of reflexion of the modified radiation (equation 5) are thus not the same as those of the unmodified radiation (equation 6) and, as will be shown presently, the difference between them is such that if the radiation scattered as modified radiation by a substance in the amorphous form was regularly reflected by a crystal of the substance according to (5) the phenomenon would have been detected experimentally. For such detection (1) the modified and unmodified beams must be resolvable; (2) the intensity of the modified beam must be sufficient.

The separation of the incident modified and unmodified rays corresponds to a wave-length interval of $\cdot 024 \text{ Å}$ (*cf.* equations (5) and (6)), which is six times the difference between the $K\alpha_1$ and $K\alpha_2$ lines of rhodium. The rhodium $K\alpha_1$ and $K\alpha_2$ lines can, however, be resolved by a spectrometer of moderate resolving power, so that the modified beams certainly satisfy the condition of resolution.

In order to discuss the second condition we shall take the particular case of a rock-salt crystal and consider the reflexion from planes having the structure factor $\text{Na} + \text{Cl}$ of order such that the glancing angle is about 30° . The angle of scattering will then be about 60° and the ratios of the energies of the modified and unmodified radiations scattered through this angle by amorphous Na and Cl are about 1 and $\cdot 5$ respectively*. If the ratio of the energies of the reflected modified and unmodified beam was of this magnitude, *i. e.* $\cdot 5$ to 1, the modified beam would be sufficiently intense to be easily

* These values are computed from results of observations on neighbouring elements made by Compton, Ross, and others.

observed *. The intensity of reflexion depends on the sizes of the orbits which the scattering electrons describe. The larger the orbit the less in general is the contribution to the intensity of reflexion, and as there are reasons to believe that the outer electrons are mostly responsible for the modified rays, it follows that the ratio of the intensity of the modified reflected beam to that of the unmodified beam would be less than the ratio of the intensity of the modified radiation to that of the unmodified radiation scattered through the same angle by the same substance in the amorphous form. This effect of the distribution of the two radiations between the various classes of electrons in the atom can, however, hardly affect the order of magnitude of the ratio, and as this is about unity it is practically certain that the modified radiation if reflected would be sufficient to produce a beam of detectable intensity. In all the observations which have been made on the reflexion of X-rays by crystals no radiation obeying a different law from (6) has been detected. It is concluded, therefore, that the second alternative mentioned in § 1 cannot be admitted, and we are led to the first which states that no modified radiation is reflected by a crystal † ‡. The bearing of this result on the theory of the intensity of reflexion by crystals will now be considered.

§ 3. *The Compton Effect and the Intensity of Reflexion.*

The conclusion arrived at in the last paragraph admits two alternatives :

(a) No modified radiation is scattered by the electrons in the directions of regular reflexion.

(b) Modified radiation is scattered by the electrons in the same way as if they belonged to amorphous material, but is not regularly reflected.

It would seem at first that the orderly arrangement of atoms, which characterizes crystals, ought not to influence the initial scattering by the individual electrons and that (a) could accordingly be dismissed. However, the phenomenon

* The $K\alpha_1$ line of rhodium possesses only a third of the energy of the $K\alpha_2$ line and is quite prominent, though separated from the $K\alpha_2$ line by a much smaller angle than that which would separate the modified $K\alpha_1$ line from the unmodified $K\alpha_1$ line.

† This conclusion depends of course on the validity of the method used to derive the laws of reflexion of the modified radiation.

‡ Kallmann and Mark (*loc. cit.* p. 134) have independently arrived at this conclusion by a process of reasoning essentially the same as that used here.

of reflexion from crystals is one in which the electrons cooperate in the scattering, and it may be possible that this cooperation means a big increase in the effective mass of the scattering electrons in so far as encounters between them and the incident quanta are concerned. The change of wavelength, being inversely proportional to the mass of the scatterer, would consequently be much smaller than that which ordinarily characterizes the modified radiation. In other words, the modified radiation, when reflected, automatically becomes "unmodified," owing to the increase in the effective mass of the scattering electrons. If the "modified" radiation becomes sufficiently "unmodified" as to be able to interfere with the ordinary unmodified radiation, the classical theory of the intensity of reflexion needs no revision. It may be, however, that this is not so, in which case there is an effect on the intensity of reflexion. This possibility will not be discussed any further at present, and the effect on the intensity of reflexion will be considered on the basis of the second alternative (b).

According to (b) the amplitudes of the modified and unmodified waves due to the individual electrons in the crystal are the same as they would be if the electrons belonged to amorphous material, and the amplitude of the reflected wave is the vector sum of the amplitudes of the unmodified waves*. The intensity of reflexion will evidently be different from what it would be if all the scattered radiation was capable of

* The number of unmodified quanta that leave a crystal in the direction of reflexion is considerably greater than the number that would leave an amorphous body in that direction. The radiation scattered by an amorphous body is symmetrically distributed about the forward direction so that the momentum communicated to the body from the radiation is in this direction. In terms of the quantum theory this means that the directions of recoil of the scatterers are symmetrically distributed about the forward direction. In the case of reflexion by a crystal, the resultant momentum imparted to the crystal as the result of scattering is not in the forward direction but has a component perpendicular to the reflecting planes as well as a forward component. On the quantum theory this means that there is a preponderance of scattering bodies which recoil with components normal to the reflecting planes (on the side remote from the incident and reflected beams). In view of this we must suppose that the reinforcement of the scattered waves in the direction of reflexion influences the encounters between the quanta and electrons in such a way that a preponderance of quanta leave the electrons in the direction of reflexion, and the dynamical conditions of such encounters may be supposed to be the same as those holding in the case of the much lesser number of unmodified quanta that would be scattered in the same direction were the substance amorphous. This influence must not be confused with that discussed in connexion with (a). The supposition made there is that the reinforcement giving rise to regular reflexion increases the effective masses of the electrons.

being reflected, and the effect will now be considered more in detail.

The formula for the intensity of X-ray reflexion involves quantities, F , which represent the ratios of the amplitude of the wave scattered by an atom as a whole to that of the wave scattered according to the classical theory by a single electron. These are the quantities the estimated values of which have to be revised in order to allow for the non-reflexion of the modified radiation*. The revised values, which we shall denote by F_u , represent the ratio of the amplitude of the unmodified wave scattered by an atom to the amplitude of the wave which a single electron would scatter according to the classical theory, and these values have been calculated for the atoms of certain elements.

A calculation of F_u requires a knowledge of the relative amounts of the modified and unmodified scattered radiations respectively†. G. E. M. Jauncey‡ has developed a quantitative theory of this partition of energy in the case of scattering by amorphous substances. The theory is based on the criterion, first suggested by A. H. Compton, that if a quantum does not give sufficient energy to the electron which scatters it to enable the electron to leave the atom, the quantum is unmodified.

It should be mentioned, however, that the general nature of the differences between the revised F curves and the classical curves can be deduced directly from the results of observations on the relative intensities of the modified and unmodified radiations scattered by different elements in the amorphous form, and the correction for the Compton effect is to this extent independent of Jauncey's theory.

Jauncey's theory refers to, and all observations have been made on, the *energies* of the two types of scattered radiation, whilst the quantity which is directly concerned in interference phenomena is the amplitude of the radiation. Let us consider a single electron and let j be the fraction of the energy scattered in a given direction which is unmodified, leaving a fraction $1-j$ of modified radiation. Now the coefficient of

* The values of F according to the classical theory have been calculated by D. R. Hartree, *Phil. Mag.* vol. 1. p. 289.

† The allowance for the Compton effect cannot be made directly from a knowledge of the fraction of the radiation that is unmodified when the substance is in the amorphous form. The relative amounts of unmodified and modified radiations are different for electrons belonging to different orbits, and as the diffraction effect is also different for the different orbits it is obvious that the correction has to be made separately for the various orbits.

‡ *Phys. Rev.* (2) xxv. pp. 314, 723 (1925).

total scattering (including the modified and unmodified radiations) from light elements in the amorphous form, in which case the electrons scatter independently, obeys the classical theory *. Therefore, if the energy of the scattered radiation from a single electron according to the classical theory be denoted by unity, the absolute values of the energies of the unmodified and modified radiations are j and $1-j$ respectively. The energy of radiation is proportional to the square of the amplitude, and taking the constant of proportionality as unity the amplitude of waves scattered according to classical theory will be unity. Actually there are two trains of scattered waves representing energies j and $1-j$ respectively. In deducing the relation between the energies and amplitude there are two alternative suppositions which can be made and which lead to slightly different results. We can suppose that the electron is simultaneously scattering the two types of radiation having relative energies in the ratio of j to $1-j$, or alternatively, that the two radiations are scattered intermittently, the aggregate times being in the ratio of j to $1-j$. On the first assumption the amplitudes of the unmodified and modified waves scattered by a single electron are $\sqrt{j}$ and $\sqrt{1-j}$ respectively. According to the second, unmodified waves of unit amplitude will be scattered for a fraction j of the time and modified waves of unit amplitude for a fraction $1-j$ of the time, and as far as reflexion is concerned this state of affairs is equivalent to simultaneous scattering in which the amplitudes of the unmodified and modified waves are j and $1-j$ respectively. Revised values (F_u) of F have been calculated on the basis of each of the two suppositions. The value of F_u obtained on the first supposition will be denoted by F_{u_1} , and that on the second supposition by F_{u_2} .

The value of j according to Jauncey's theory depends on the ionization energy of the electron, the magnitude and direction of its orbital velocity, the wave-length of the X-rays, and the glancing angle, β . The dependence on the last two quantities is a function of $\sin \beta/\lambda$, so that β and λ are not involved separately. If B^2 and ϵ denote the orbital kinetic energy and ionization energy respectively of an electron for which all directions of motion are equally likely, then j is given by

$$j = .5 + \epsilon/4B\psi - \psi/4B, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\psi = 2h/mc \times (\sin \beta/\lambda)$.

* This applies to neither of the two radiations separately, the relative intensities of the modified and unmodified radiations varying considerably with wave-length and angle of scattering.

The value of j will be different for different orbits, and in the case of non-circular orbits will be different for different parts of the orbit *. The same applies to the diffraction effect and in calculating the values of F_u the different orbits in the atom have been considered separately, and in the case of non-circular orbits the different elements of the same orbit. Hartree † shows, in a paper on "The Atomic Structure Factor in Crystal Reflexion," how to calculate the values of F on the classical theory. In calculating the revised values considerable use has been made of tables given in this paper. Data relating to the potential field of certain atoms have also been kindly given to the writer by Mr. Hartree.

§ 4. Discussion of "F" Curves.

The values of $F_{c\ddagger}$, F_u , and F_{u_2} for different values of the glancing angle β , for the calcium ion (Ca^{++}) and the fluorine ion (F^-) are given in Table I., the values of $\sin \beta$ corresponding to the wave-length Rh.K α rays ($\lambda = 0.614 \text{ \AA.}$). Stoner's distribution of electrons has been assumed.

TABLE I.

$\sin \beta$ ($\lambda = 0.614 \text{ \AA.}$)	Ca^{++}			F^-		
	F_c	F_{u_1}	F_{u_2}	F_c	F_{u_1}	F_{u_2}
0.00	18	18	18	10	10	10
0.10	15.6	14.4	13.3	8.4	6.9	5.7
0.20	11.1	10.0	9.1	5.2	3.2	2.5
0.30	8.5	8.0	7.0	2.7	2.0	1.8
0.40	8.4	6.9	5.7	1.2	1.7	1.4
0.50	7.8	5.8	4.7	.6	1.5	1.2
0.60	6.3	4.9	3.9	1.0	1.3	1.0
0.70	5.0	3.9	3.1	1.8	1.1	.80

The results are shown graphically in fig. 1 together with curves which represent the observed values of F deduced

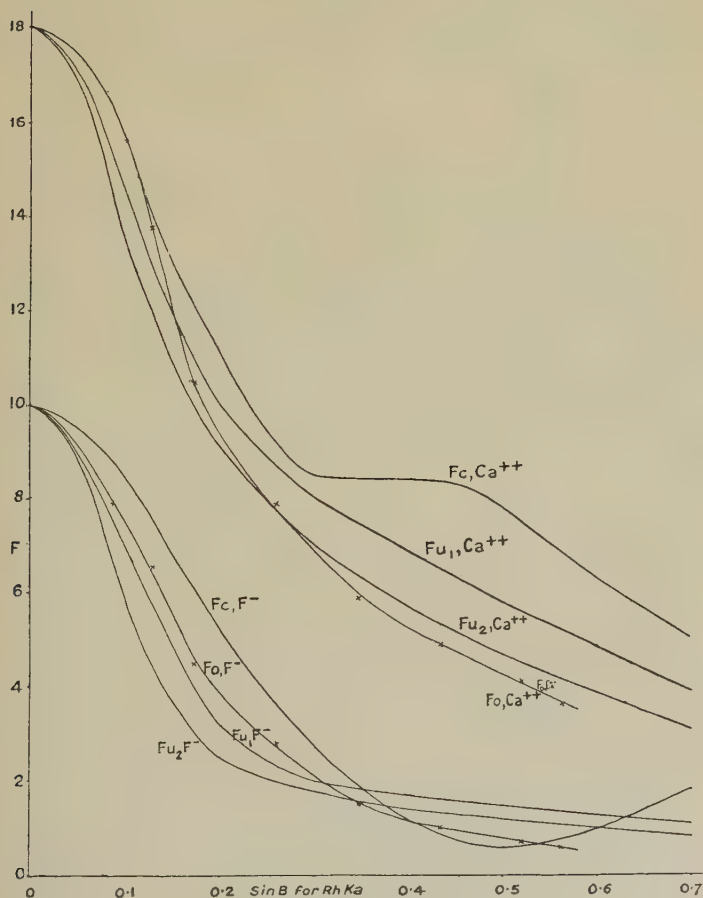
* In so far as the calculation of F is concerned, a circular orbit is equivalent to a spherical shell of electricity, and the effective value of j may be different for different parts of the same shell, being equal at any point to the value given by Jauncey's theory for an electron confined to move in the plane tangential to the sphere at that point. Such a possibility has not been allowed for in the present calculations, as an allowance for it would have little effect on the numerical results, there being in fact no effect when j for the whole orbit has the values 0, .5, and 1.

† *Loc. cit.*

‡ The values of F_c for Ca^{++} are taken from Hartree's paper (*loc. cit.*), and those for F^- have been calculated by Hartree's method.

from the actual intensity of reflexion by James and Randall*, using the reflexion formula. These curves will now be compared.

Fig. 1.



i. Order of magnitude of difference between the Curves.

The difference between the F_c and F_u curves is quite appreciable in certain regions, the maximum difference between the values of F_c and F_u , in the case of calcium, for instance, being about 25 per cent., whilst the values of F_{u1} for fluorine are in some places only half those of F_c and in

* James and Randall, Phil. Mag., May 1926.

other places are twice those values. The difference between F_c and F_{u_2} is still greater but is everywhere in the same direction, the curves F_{u_1} and F_{u_2} being very similar. The revision of the values of F has, however, not produced a radical departure from the classical values. Had the revision resulted in such a difference there could not be any agreement between the revised values and the observed values.

ii. Initial Values.

The values of F_c and F_u are seen to be the same at zero glancing angle, being equal to the number of electrons in the ion. It can be readily seen why this should be the case. For when the angle of scattering is zero the momentum communicated to the scattering electron is zero and the electron cannot possibly be ejected from the atom. As this is the condition for modification, it follows that all the radiation scattered in the forward direction is unmodified, and consequently the values of F_u and F_c are the same.

This result is not entirely dependent on Jauncey's theory, but can be deduced in a general way from the observed intensities of the unmodified and modified radiations. These show that the relative intensity of the modified radiation falls off quickly with decreasing angle of scattering and would indicate that at zero glancing angle there would be no modified radiation scattered, thus making $F_u = F_c$ as above.

The actual values of F at zero glancing angle or extremely small glancing angles cannot of course be obtained from observations on the intensity of reflexion, as there are no reflexions at glancing angles less than about $\sin^{-1} .1$. As a result of determinations of the absolute values of F for Na and Cl at this and bigger angles, Bragg, James, and Bosanquet* concluded, however, that "the values for F when $\sin \beta = 0.1$ are of the order to be expected if the curves for chlorine and sodium have maxima at about 18 and 10 respectively." These numbers are the theoretical maximum values of F , being the respective numbers of electrons in the two ions.

In the determination of the "observed" values of F for Ca and F, James and Randall† chose a value of the extinction coefficient which made the observed value for Ca at $\sin \beta = 0.1$ coincide with the value calculated by Hartree on the classical theory. These authors show that the value

* W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.* (6) xli. p. 334.

† *Loc. cit.*

for the extinction obtained in this way leads to consistent results when intensities of reflexion for planes with structure amplitudes $\text{Ca} + \text{F}_2$, Ca , $\text{Ca} - \text{F}_2$, are compared, thus showing that the value must be nearly correct. In comparing the F curves in fig. 1 it must, therefore, be realized that James and Randall have made F_c and F_o coincide at the smallest glancing angle at which reflexion is observed, and that the better agreement between F_c and F_o than between F_{u_1} or F_{u_2} and F_o for small angles is not necessarily real.

iii. *Flattening of F curve for Ca^{++} in region of $\sin \beta = .35$, and Rise in F curve for F^- after $\sin \beta = .5$.*

The classical F curves do not fall off uniformly with increasing glancing angle over the whole range under consideration, and in this respect differ from the observed curves and the revised curves. In the case of calcium there is a distinct sudden flattening of the F_c curve in the region around $\sin \beta = .35$, and in the case of fluorine the F_c curve begins to rise after $\sin \beta = .5$. The reasons for the presence of these characteristics in the F_c curves and their absence in the revised curves can be made clear in a general way as follows.

The contribution from the outer orbits 3_1 and 3_2 in the case of calcium⁺⁺ falls off very rapidly with $\sin \beta$ and then oscillates in value, passing through a negative minimum value at $\sin \beta = .33$, and a positive maximum at $\sin \beta = .48$. In the case of fluorine the contribution to F from the outer orbits 2_1 and 2_2 reaches a minimum value at $\sin \beta = .5$ and then rises again. This oscillation is due to the relatively large sizes of the outer orbits and is absent in the contributions from the inner electrons in the region of glancing angles considered. This oscillating nature of the contribution from the outer electrons is directly responsible for the flattening of the F_c curve for calcium at $\sin \beta = .35$ and the rise in the F curve for fluorine after $\sin \beta = .5$. Now when we come to consider the values of F_u , we find that as the outer electrons are also more loosely bound the amount of unmodified radiation scattered by them falls off rapidly with increasing glancing angle, with the result that the contribution to F_u from these electrons is small, and does not affect the uniform falling off of the F_u curve for the whole atom*. This result is not wholly dependent on

* In fact the contribution that these electrons do give to F comes from the parts of the orbits close to the nucleus, and therefore possesses none of the characteristics resulting from large radial distances from the nucleus.

Jauncey's theory. The results of observations on the relative intensities of the modified and unmodified radiations scattered from elements of different atomic numbers show that the more loosely bound the electrons are to the atom the less unmodified radiation they scatter, and therefore the contributions to F from outer electrons must be relatively unimportant.

The above argument applies to all atoms and we can state, as a general result, that the classical F curve for an ion does not fall off uniformly with increasing glancing angle owing to the oscillating nature of the contributions from the outer electrons. In the case of moderately heavy atoms, such as Cl, K, and Ca, there is a distinct flattening of the F_c curve when F is about half its maximum value, and for light atoms, such as O and F, the curve passes through a minimum and then rises. On the other hand, the F_u curves for these atoms fall off uniformly because the contribution to F_u from the outer electrons is negligible in the region of glancing angles concerned. There is no evidence of these characteristics in the "observed" curves, and in this respect the agreement between the revised F curves and the observed curves is much better than that between the classical F curves and the observed curves.

iv. *Values of F at relatively large angles.*

The "observed" values of F are not corrected for the Debye temperature effect. This effect is almost negligible at small glancing angles and becomes appreciable only at large glancing angles. The correction would somewhat increase the "observed" values at large angles and would improve the agreement between them and the values of F_u .

v. *Dependence of correction for the Compton Effect on wavelength and glancing angle.*

It has already been pointed out that the relative amplitudes of the modified and unmodified radiations do not depend on β and λ separately but are functions of $\sin \beta/\lambda$. This is so because the criterion for scattering with or without modification involves β and λ only in so far as they control the momentum imparted to the scattering electron, which is represented by $2hc \times (\sin \beta/\lambda)$. It is interesting to note that the correction for the Compton effect thus resembles other factors which determine the values of F , and that a curve in which F is plotted against $\sin \beta/\lambda$ will hold for all wavelengths.

§5. *Power of a Crystal to reflect the modified and unmodified radiations scattered by its electrons.*

According to the prevailing theories of the Compton effect (due to Jauncey*, Bohr, Kramers, and Slater†) there is no fundamental difference between the production of the modified scattered radiation and that of the unmodified scattered radiation. The difference is incidental and depends on whether the scattered quantum gives sufficient energy to the scattering electron to enable it to leave the atom or not. Certain experimental facts also add conviction to this view. The relative intensities of the modified and unmodified scattered radiations vary considerably with wave-length and scattering angle‡. Nevertheless, the magnitude of the coefficient of *total* scattering is independent of the wave-length over a large range, and the variation of the intensity of *total* scattering with scattering angle obeys the simple " $1 + \cos^2 \theta$ " law. It follows that a decrease in the intensity of one type of radiation is always accompanied by a balancing increase in the intensity of the other. The two radiations are thus intimately dependent on one another, and hence cannot be produced by two fundamentally different processes. The reason for a state of affairs as described in §3(b) must therefore be found in minor differences between the two types of radiation. According to the above theories the "unmodified" scattered radiation is strictly speaking modified, the change of wave-length being, however, very small compared with that experienced by the "modified" radiation. The change in frequency of a quantum due to scattering is inversely proportional to the mass of the scattering body, and the theoretical change in the "unmodified" radiation, which on these theories is the result of encounters between quanta and atoms, is too small to be detected, being of the order of 10^{-6} Å. Nevertheless there is on these theories a change, and the difference between the modified and unmodified scattered radiations must be regarded as one of degree only. The question is whether this difference in degree can account for the non-reflexion of the modified radiation. In order to consider this question it is necessary, as

* *Loc. cit.*

† Bohr, Kramers, & Slater, *Phil. Mag.* [6] xlvii., 1924.

‡ The number of recoil tracks produced in oxygen, for instance, shows that at least 80 per cent. of the scattered radiation ($\lambda = 0.61$ Å) is modified, whilst the spectrum of the radiation scattered by graphite through small angles shows a predominance of unmodified radiation.

it was in the discussion of the laws of reflexion of the modified radiation, to use the wave theory and assume hypothetical scatterers moving in such a way as to give the necessary change in wave-length. Compton* showed that the change in wave-length of the modified radiation follows as a Doppler effect if we assume the scattering electrons to be moving in the direction of the incident rays with a velocity $h/m\lambda$. In calculating the change in wave-length required by the quantum theory of scattering, Compton did not take into account the motion of the scattering electrons in their orbits. Jauncey subsequently extended the theory so as to take into account this motion, and showed that the change of frequency of the scattered quantum depends on the magnitude and direction of the velocity of the scattering electron at the instant of scattering, the change in wave-length being given by

$$\delta\lambda/\lambda = 2h \sin^2 \theta/2 / mc\lambda + 2u \sin \theta/2 \cdot \cos \phi/c, \quad (8)$$

where u is the magnitude of the orbital velocity of scattering electron and ϕ is the angle it makes with the momentum lost by the quantum. It follows from (8) that a single wave-length primary radiation should be scattered as a "band," different changes of wave-length being due to different values of ϕ and u . This is in accordance with observations, and Jauncey has shown that the extent of the observed "broadening" of the modified line is also quantitatively in agreement with the theory. In view of this effect it is not correct to assume a uniform drift of the hypothetical scatterers. These scatterers must be assumed to be moving with various different velocities, the range of velocities corresponding to the range of wave-lengths in the modified radiation. There are two hypotheses which can be made as regards this motion. We can associate a hypothetical scatterer with each electron in the crystal, the velocity of the hypothetical scatterer at any instant being that which would give the change of wave-length required by (1), u and ϕ referring to the corresponding electrons at that instant, or, we can regard the hypothetical scatterers as belonging to a multitude of classes, all the scatterers in the same class moving with the same velocity and therefore maintaining fixed relative positions. The first of these hypotheses will be made the basis of the present argument.

Let the vector w_0 be the velocity which gives a Doppler change of wave-length equal to that represented by the first

* *Loc. cit.*

term in (8), and let w be the velocity which gives a change of wave-length represented by the second term. Then a velocity $w_0 + w$ will give the complete change of wave-length required by (8). w_0 is the same for all the electrons concerned, so that the relative positions of the scatterers are not affected by this component of the velocity. The value of w , however, depends on u and ϕ , which continually vary as an electron moves in its orbit, so that u and ϕ at any instant may be different even for electrons describing similar orbits, and therefore w at any instant is different for the different hypothetical scatterers. Now if at any time, t_0 , we suppose the relative positions of the scatterers to be the same as those of the electrons in the crystal to which they correspond, this will not be the case at any subsequent instant because of the variation in w . The component w_0 , as already mentioned, does not affect the relative positions and can be left out of account. The important quantity is $\int_{t_0}^t w dt$ which represents the distance, at time t , of a scatterer from its mean position*. The same argument as the foregoing applies to the unmodified radiation, the only difference being that instead of (8) we have a similar equation with the mass of the atom and its velocity of thermal agitation, instead of the mass of the electron and its orbital velocity respectively. The velocity of the hypothetical scatterers associated with electrons which scatter unmodified quanta can then be represented by $W_0 + W$, where W_0 is constant and W variable, and their displacement from their mean positions is given by $\int^t W dt$. We have now two systems of scatterers, the one moving with a uniform velocity w_0 , its individual scatterers being at any instant at a distance $\int^t w dt$ from their mean positions; the other moving with uniform velocity W_0 , the instantaneous displacement of its scatterers from their mean positions being $\int^t W dt$. The first system scatters modified radiation, the second unmodified radiation. Now, let us suppose that the value of $\int_0^t w dt$ is large compared with the wave-length, λ , of the X-rays, and that $\int_0^t W dt$ is small compared with λ . Then, in the first case the magnitude of the oscillation of the scatterers about their mean

* If $\lim_{t \rightarrow \infty} (\int_0^t w dt)/t$ is not zero (and equal to w_0' say), then $\int^t w dt$ does not represent the distance from the mean positions and it must be replaced by $\int_0^t (w - w_0') dt$.

position will reduce the amount of regular reflexion to a negligible value and no modified radiation is reflected, whilst in the second case it only causes a small decrease in the intensity of the reflexion so that the unmodified radiation is still reflected. In the present state of theory it is impossible to calculate the values of $\int W dt$ and $\int w dt$ without making several and very arbitrary assumptions, and such a calculation will not be attempted here. This discussion has, however, indicated a plausible way of accounting for the state of affairs represented by § 3 (b).

Summary.

The laws which would apply to the reflexion by a crystal of modified radiation scattered by its own electrons are derived by considering an electron lattice moving with a velocity that would give as a Doppler effect the change in wave-length demanded by the quantum theory of scattering. The difference between these and the ordinary Bragg laws of reflexion is appreciable, and as all the radiation actually reflected obeys Bragg's law it is concluded that (a) no modified radiation is scattered by the electrons in the directions concerned, or (b) modified radiation is scattered but is not regularly reflected. The bearing of the Compton effect on the theory of the intensity of reflexion by crystals is considered on the basis of the second alternative, and an outline of the way in which revised "F-curves" have been calculated is given. The "classical" F-curves, the revised curves, and the "observed" curves are compared. The revised F-curves are little influenced by the contribution from the outer electrons because these electrons scatter very little unmodified radiation, and as a result they agree much better than the classical curves with the curves actually observed. The correction for the Compton effect is a function of $\sin \beta / \lambda$, and in this respect resembles other factors entering into the theory of the intensity of reflexion.

The capacity of a crystal to reflect modified and unmodified radiation is discussed. There is no fundamental difference between the modified and unmodified radiations, and reasons for the incapacity of a crystal to reflect the modified radiation scattered by its electrons (if that is the case) must be based on minor differences between the two.

In conclusion I wish to thank Professor W. L. Bragg, F.R.S., for bringing the subject of the present investigation to my notice and for the kind interest which he has taken in the work.

APPENDIX.

The contribution to the value of F_u for the calcium ion from the electrons belonging to the 2_2 orbit will be considered in order to illustrate the way in which the revised values of F have been calculated. Hartree has shown that a circular orbit is equivalent, as far as the diffraction effect is concerned, to a spherical shell of electricity of radius equal to that of the orbit, and if all the radiation scattered was unmodified the contribution to F_u for each electron describing an orbit of this type would be that corresponding to a single stationary electron multiplied by the factor

$$\int_{-a}^{+a} \cos(4\pi x \sin \beta / \lambda) \frac{dx}{2a}, \text{ which we shall denote by } C(\beta).$$

The radius of the 2_2 orbit of calcium according to Hartree's formula (*loc cit.* p. 299) is $\cdot 134 \text{ \AA}$, and the values of $C(\beta)$ for different values of the glancing angle, β , are given in the second column of the accompanying table. All the radiation scattered is, however, not unmodified, and the effective

TABLE II.

Contribution to F_u for Calcium from electrons belonging to the 2_2 orbit.

$\sin \beta$.	$C(\beta)$.	j .	$\sqrt{j}$.	$6 \times C(\beta) \times j$.	$6 \times C(\beta) \times \sqrt{j}$.	$6 \times C(\beta)$.
0	1.00	1.00	1.00	6.00	6.00	6.00
.1	.98	1.00	1.00	5.88	5.88	5.88
.2	.95	.84	.92	4.74	5.22	5.70
.3	.89	.67	.82	3.54	4.38	5.34
.4	.81	.57	.75	2.76	3.66	4.86
.5	.70	.50	.71	2.10	3.00	4.20
.6	.51	.44	.66	1.62	2.40	3.66
.7	.47	.39	.62	1.08	1.74	2.82

amplitude of the unmodified wave scattered by an electron is less than unity, being equal to j or $\sqrt{j}$ according to the supposition made as regards the nature of the scattering, j being the fraction of the scattered energy in the unmodified rays. In the present calculations j has been taken constant over the equivalent spherical shell, having a value equal to that given by Jauncey's theory for the whole orbit (equation 7). The value of j depends on the binding energy and orbital kinetic energy of the electron as well as on the wave-length and scattering angle of the rays. The values of the binding energy and orbital kinetic energy of electrons belonging to the 2_2 orbit

of a calcium atom are approximately 400 and 1000 volts respectively (computed from values given by Hartree for atoms of neighbouring elements), and the values of j or $\sqrt{j}$ are given in columns (3) and (4) of the table. In order to obtain the contribution to F_u the amplitude of the unmodified wave leaving the electron must be multiplied by the diffraction factor, $C(\beta)$. According to Stoner there are six electrons describing 2_2 orbits in the calcium atom, and the contribution δF_u to F_u from this class of electrons is therefore $6jC(\beta)$ or $6\sqrt{j}C(\beta)$, according to the supposition made as regards the nature of the scattering. The values of δF_u are given in the fifth and sixth columns. The contributions to F on the classical theory are given in the last column for comparison.

In the case of elliptic orbits different elements of the orbit defined by the distance of the electron from the nucleus have been considered separately, the calculation for each element being similar to that for a circular orbit. The value of F_u for the whole ion is obtained by adding up the contributions, δF_u , from the various classes of electrons in the ion.

LIX. *Radiation produced by the Passage of Electricity through Gases.* By Sir J. J. THOMSON, O.M., F.R.S.*

IN the Philosophical Magazine for May 1925 I gave an account of experiments which showed that the passage of the electric discharge through gases at low pressures gives rise to the emission of radiations which, like radiation in the extreme ultra-violet or very soft X-rays, are absorbed with such rapidity that they cannot penetrate more than a thin layer of gas unless the pressure is very low; as they give rise to very intense ionization, they are of fundamental importance in the theory of the electric discharge through gases. In this paper I describe a series of experiments on the sources and characteristic properties of these radiations.

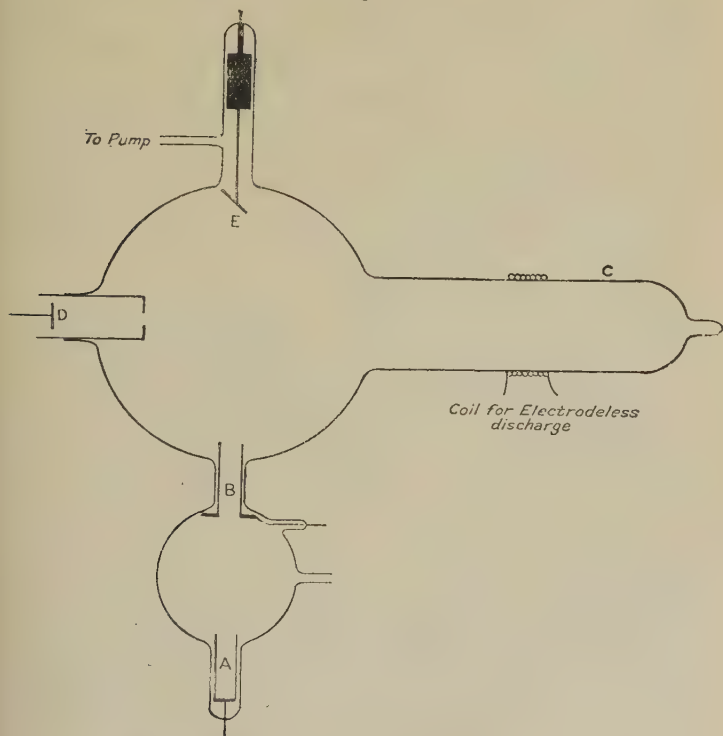
The experiments described in the earlier paper were made on the radiation coming from the space between the anode and cathode of a discharge-tube; in this region there are both moving electrons and moving positive ions, and their radiations are superposed. In the following experiments the effects due to the electrons and the positive ions were studied separately. For this purpose streams of either cathode or positive rays were isolated and sent past the window through

* Communicated by the Author.

which the radiations passed to the apparatus by which they were detected and tested.

The electrodes A and B (fig. 1) for the discharge were placed at one end of a long tube. B is a brass or aluminium cylinder fitting tightly into the glass tube; a hole is bored out along the axis of this cylinder. A was in some cases a plane disk with its plane at right angles to the axis of B;

Fig. 1

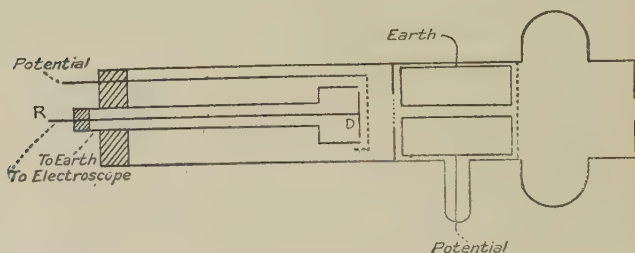


in other cases it was a tube whose axis was in the same straight line as the axis of B. When A is made cathode a beam of cathode rays, and when it is made anode a beam of positive rays, streams through the boring in the cylinder B and excites radiation in the gas. This radiation is detected by the photoelectric effect it produces when it falls upon a polished metal disk D which is connected with a Dolezalek electrometer. In order to screen off from the disk the effects which would be produced by ions diffusing from the discharge-tube two methods have been employed, which

are described on pp. 769 and 762, *Phil. Mag.* xlix. (1925). In the first of these methods the ions are stopped by a strong electric field and the radiation has not to pass through any solid obstacle, but passes through a slit between two half-cylinders insulated from each other and connected with the terminals of a battery of storage cells; there is thus a strong electric field across the slit. The geometry of the apparatus was such that the beam of rays was parallel to the slit and was in full view of the disk D. The details of the electrical connexions and the position of screens of wire gauze to screen off any electrostatic effects due to the charges on the half-cylinders are indicated in fig. 2.

The efficiency of the screen for stopping the ions and electrons coming from the discharge was tested by increasing the potential difference between the half-cylinders. With the potentials used this increase produced no change in the deflexion of the electrometer, nor was any difference

Fig. 2.



produced by reversing the direction of the field between the slits.

The other method used to screen off the ions is to place the disk D in a brass tube with a very thin celluloid window at one end; the celluloid stops the ions, but allows some of the radiation to get through. I showed in the previous paper that even the thinnest celluloid obtainable stops all but a small fraction of the soft radiation coming from the tube.

Special precautions were taken to isolate the radiation coming from the molecules of the gas from that due to the impact of the electrons or positive rays against the walls of the discharge-tube. A side tube C (fig. 1) about 20 cm. long and 5 in diameter was used on to the main tube opposite to the testing apparatus, and the slit between the cylinders used to produce the screening electric field stopped down until the only part of the glass of the tube visible from the

photoelectric disk was that at the far end of the tube C, which is far out of the path of the electrons.

The intensity of the stream of cathode or positive rays is estimated by the charge they give to the disk E (fig. 1), which is connected to earth through a high-resistance galvanometer. The disk can be moved backwards and forwards down the tube and can be brought within view of the disk connected with the electrometer; when in this position the radiation due to the impact of the rays against the disk E, as well as that coming from the molecules of the gas, falls upon the testing apparatus, and by comparing the effects when E is in this position with those when it is pushed back we can estimate the relative intensities of these radiations.

Radiation due to the passage of cathode rays through the gas.

When the electrode A (fig. 1) was the cathode and a stream of cathode rays went through the opening in B past the window leading to the testing apparatus, the electrometer received a continuously increasing positive charge; this we ascribe to the ejection of electrons from the disk connected with the electrometer, due to the incidence of the radiation excited by the cathode rays in their course through the gas. If the stream of cathode rays is deflected by a magnet so that it can no longer be seen from the disk connected with the electrometer, the deflexion of the electrometer ceases, showing that the radiation came from the gas traversed by the beam of cathode rays and not from the walls of the tube.

If the target E is moved down the tube until it comes within sight of the disk connected with the electrometer so that the radiation excited by the incidence of the cathode rays on the metal target falls upon the disk, the deflexion of the electrometer is increased greatly, sometimes more than a hundredfold.

Radiation excited by positive rays.

When A (fig. 1) is made anode a beam of positive rays passes through the gas in sight of the disk connected with the electrometer, the electrometer acquires a continuously increasing charge of positive electricity, showing that the passage of positive rays through the gas excites radiation. In fact, when the electric discharge is produced by an induction coil the deflexion of the electrometer is greater when the induction coil is arranged to send a beam of positive rays through the tube than when the coil is

reversed, so that cathode rays pass in front of the window. The number of positive and cathode rays passing past the window in unit time can be ascertained from the deflexions of the galvanometer which connects the target E (fig. 1) with the earth. Knowing the number of rays and the deflexion of the electrometer, we can calculate the deflexion due to one cathode or one positive ray. The result depends upon the nature of the screen used. When the ions are screened off by the electric field, the deflexion due to one positive ray is greater than that due to one cathode ray; when they are screened off by a celluloid film, the deflexion due to a cathode ray is much greater than that due to a positive one. This is, I think, due to the fact that the radiation produced by the positive rays is less penetrating than some of that produced by the cathode ones, so that a much larger proportion of the positive radiation than of the negative is stopped by the celluloid window.

Just as with cathode rays there is a great increase in deflexion when the target is brought forward, so that radiation from it can reach the disk connected with the electrometer; thus the impact of positively electrified particles with metal gives rise to radiation. I showed this by a photographic method many years ago.

The deflexion of the electrometer produced when the target is moved so as to be in sight of the disk connected with the electrometer is in general a larger multiple of the deflexion without the target when the celluloid film is used than with the electrostatic screen. This is, I think, due to the fact that in the latter case the opening through which the rays can pass is a very narrow one while the celluloid window has a much larger area; thus a large proportion of the rays produced by impact with the target will get through the window without any very accurate adjustment of the position of the target, while with the narrow opening only a comparatively small fraction of the rays will get through unless the target is in just the right position.

On the Nature of the Radiation produced by Cathode and Positive Rays.

I have used two methods to investigate the nature of the radiation: the first was to measure the absorption of the metal by thin gold, or aluminium, foil, and the second was to measure the velocity of the electrons ejected from the disk connected with the electrometer when the radiation fell upon it.

Absorption of radiation by thin metallic films.

Films of thin gold and aluminium were interposed in the path of the radiation in the way described in Phil. Mag. xlix. p. 764 (1925), and the consequent diminution in the rate of charging up of the electrometer was measured. Experiments were made on the influence on absorption of the nature of the gases in which the radiation was produced, and of the difference of potential between the anode and cathode of the discharge-tube. The radiations were produced by a stream of cathode rays passing through the gas; as the celluloid window was used, the most absorbable rays were absent. The discharge was produced by a high-potential dynamo made by Evershed and Vignolles, which gave steady potential differences up to 5500 volts.

The thickness of the gold leaf was 7.2×10^{-6} cm., of the aluminium leaf 5.3×10^{-5} .

Absorption of rays by Gold leaf.

Voltage between cathode and anode.	Ratio of intensity of incident to emergent radiation when the cathode rays passed through.		
	Hydrogen.	Oxygen.	Argon.
1500	...	5.0	
2000	3.8	3.5	
2500	...	3.2	
3000	2.6	2.6	2.6
3500	...	2	2.1
4000	2	2	2.0
4500	1.7	2	
5000	{ 2.8 } { 4.0 }	1.7	1.5
5500	10	1.6	

In hydrogen the current is very unsteady at voltages higher than 4500, and the appearance of the discharge keeps changing abruptly.

Absorption of rays by Aluminium foil.

Voltage between cathode and anode.	Ratio of intensity of incident to emergent radiation when the cathode rays passed through.		
	Hydrogen.	Oxygen.	Argon.
1500	...	2.1	
2000	2.0	1.8	
2500	...	2.0	
3000	1.9	1.6	1.6
3500	...	1.4	
4000	1.4	1.3	1.7
4500	1.3	1.3	
5000	{ 1.9 } { 2.2 }	1.4	1.5
5500	8	1.3	

The absorbability of the radiation varies, however, with the kind of electric discharge used to produce it. When an induction coil is used instead of a continuous-current dynamo, the radiation becomes less penetrating even though the length of the equivalent spark-gap may show that the maximum difference of potential produced by the coil is greater than that produced by the dynamo.

We see from the above table that the penetrating power of the radiation generated by the cathode rays increases with the velocity of the rays, though not nearly so quickly as it would if the frequency of the radiation were proportional to the energy of the rays. It does not seem to vary much with the nature of the gas; we shall see, however, that the more absorbable radiations, especially those due to positive rays which cannot penetrate the celluloid film, do vary from one gas to another. The penetrating power of the radiation from the gas was found to be much the same as that of the radiation produced when the same rays were allowed to fall upon a target.

The absorption method of measuring the qualities of the radiation is not applicable to the very easily absorbed radiation which cannot penetrate the thinnest metal foil available, and it is this radiation which is the most important of all in connexion with the theory of electric discharge. I have endeavoured to determine the frequency of this radiation by measuring the velocity of the electrons ejected from a metal plate by the photoelectric action of the radiation. To interpret these experiments it is necessary to consider the theory of the ejection of electrons owing to the photoelectric effects of monochromatic light.

Distribution of energy among the electrons emitted from a plate by photoelectric action.

Let homogeneous radiation fall perpendicularly on a plate of metal, let the mean free path in the metal of the quantum of radiation be λ , then the chance that a quantum is absorbed at a distance between x and $x + \delta x$ from the surface of the metal is proportional to

$$e^{-\frac{x}{\lambda}} \frac{\delta x}{\lambda}.$$

If all directions of projection of the electron by the quantum are equally probable, the chance that the electron is projected in a direction making an angle between θ and $\theta + \delta\theta$ with the normal to the plate is

$$\frac{1}{2} \sin \theta \cdot \delta\theta;$$

hence the chance that an electron should start from between x and $x + \delta x$ in a direction between θ and $\theta + \delta\theta$ is proportional to

$$\epsilon^{-\frac{x}{\lambda}} \frac{\delta x}{2\lambda} \sin \theta \cdot \delta\theta.$$

If E is the energy of the electron at the beginning of its path through the metal, and E_1 the energy after it has travelled a distance l , we know that

$$E^2 - E_1^2 = \beta l,$$

where β is a constant depending upon the metal. If the electron starts from the depth x in a direction θ , the length of its path in the metal will be $x \sec \theta$ and its energy at the end

$$\sqrt{E^2 - \beta x \sec \theta} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The experimental method is to find whether the electron can escape from the metal and reach an electrode parallel to the metal plate against an opposing difference of potential V_0 .

If it is to do this, the energy due to the velocity of the electron at right angles to the plate must be not less than $V_0 e$; hence if E is expressed in the form Ve , we must from (1) have

$$\{V^2 e^2 - \beta x \sec \theta\}^{\frac{1}{2}} \cos \theta \nless V_0 e \quad . \quad . \quad . \quad . \quad (2)$$

Putting $V_0 = rV$ and $d = V^2 e^2 / \beta$, this becomes

$$d - x \sec \theta \nless dr^2 \sec^4 \theta.$$

Hence the chance of an electron being liberated by the light and escaping from the metal is proportional to

$$\frac{1}{2\lambda} \iint \epsilon^{-\frac{x}{\lambda}} \sin \theta \cdot dx \cdot d\theta,$$

where the limits of x and θ are found from the equation

$$d - x \sec \theta = dr^2 \sec^4 \theta. \quad . \quad . \quad . \quad . \quad (3)$$

Integrating with respect to x we get the term

$$\begin{aligned} & -\frac{1}{2} \left[\epsilon^{-\frac{x}{\lambda}} \right]^{d(1-r^2 \sec^4 \theta) \cos \theta} \\ & = \frac{1}{2} \left(1 - \epsilon^{-\frac{d}{\lambda}(1-r^2 \sec^4 \theta) \cos \theta} \right). \end{aligned}$$

Now d is the greatest distance the electron can travel in the metal, and if, as is usually the case, the penetrating power of the radiation is great compared with that of the electrons, d/λ will be small and the preceding expression is approximately equal to

$$\frac{d}{2\lambda} (1 - r^2 \sec^4 \theta) \cos \theta.$$

We have now to find the value of

$$\int \frac{d}{2\lambda} (1 - r^2 \sec^4 \theta) \cos \theta \sin \theta d\theta.$$

From equation (3) the limits of θ are 0 and $\cos^2 \theta = r$. Using these limits, we find that the value of the integral is

$$\frac{d}{4\lambda} (1 - r)^2.$$

Hence the rate at which the electrons escape is proportional to

$$\frac{d}{4\lambda} (1 - r)^2.$$

If the energy with which the electrons are liberated by the light quanta is E , and if opposing their escape there is an electric field of potential difference W , and if in addition it requires work measured by P volts to liberate an electron from the metal,

$$r = \frac{W + P}{E}.$$

Hence, if R is the rate at which the electrons escape from the plate,

$$R = C \frac{d}{4\lambda} \left(1 - \frac{W + P}{E} \right)^2, \quad (4)$$

where C is a quantity proportional to the intensity of the incident radiation.

Thus the graph representing the relation between R and W is a parabola touching the axis $R=0$ at the point where $W + P = E$, while that representing the relation between $\sqrt{R}$ and W is a straight line.

If the radiation is not monochromatic, then, if the intensity of the radiation having quanta with energies between E and $E + \delta E$ is $f(E)\delta E$, then R , the rate of escape of electrons from the metal when exposed to this

radiation, is given by the equation :

$$R = \int_{W+P}^{\infty} f(E) \frac{d}{4\lambda} \left(1 - \frac{W+P}{E}\right)^2 dE,$$

$$\frac{dR}{dW} = - \int_{W+P}^{\infty} \frac{d}{2\lambda} \frac{f'(E)}{E} \left(1 - \frac{W+P}{E} \right) dE,$$

and

$$\frac{d^2 R}{dW} = \int_{W+P}^{\infty} \frac{d}{d\lambda} \cdot \frac{f(E)}{E^2} dE,$$

$$\frac{d^3R}{dW^3} = -\frac{d}{2\lambda} \frac{f(W+P)}{(W+P)^2} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (4)$$

Now d and λ are functions of E . We see from equation (1) that d is proportional to E^2 , and if we suppose that the absorption of the radiation like that of Röntgen rays is proportional to the cube of the wave-length, λ varies as E^3 . On these assumptions,

$$\frac{d^3R}{dW^3} \text{ varies as } -\frac{f(W+P)}{(W+P)^3}.$$

Thus if we determine by experiment the way R varies with W and draw the graph, we can get from it the distribution of the different types of radiation in the incident light; the place where R vanishes will give the greatest frequency occurring in the radiation. If the curve is a parabola the radiation is homogeneous with this frequency, if it is not a parabola the radiation is not homogeneous; the distribution of the intensities can be determined by the preceding equation.

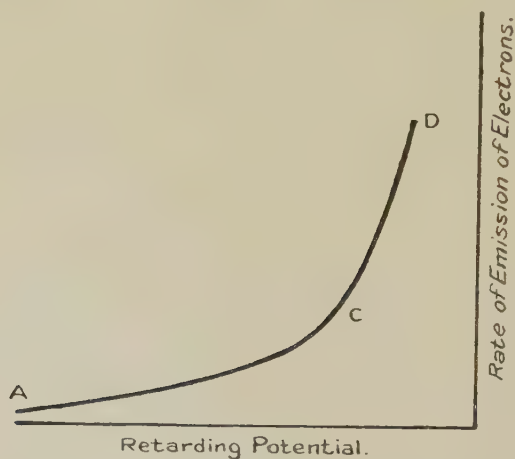
We have assumed that when an electron receives energy from a quantum of light it is as likely to start in any one direction as in any other. The justification for this is the shape of the graphs obtained by experiments.

Along any parabola whose axis is parallel to the axis of y , d^2y/dx^2 is constant and d^3y/dx^3 is zero. Hence we infer from equation (4) that when the graph (fig. 3) for the relation between the rate of emission of the electrons and the retarding potential can through a considerable stretch CD be represented by a single parabola, there is no radiation in the tube whose energy quantum is between the values of W at C and D. This gives a convenient method of determining the character of the radiation from the shape of the graph.

Thus, to take an example, if AD represents the graph, and if AC is one parabola and CD another, we know that the radiation in the tube will be of two types—one having a quantum equal to $W_A + P$, and the other to $W_C + P$, where W_A and W_C are the retarding potentials at A and C respectively, and P is the work required to extract an electron from the metal.

The relation between the rate of emission of electrons and the retarding potential will depend upon the shape of the illuminated electrode and the disposition of the retarding electric field. In our experiments the illuminated electrode was a flat plate and the retarding electric field was that between two parallel plates. If the retarding electric field

Fig. 3.



had been, as in Prof. Richardson's experiments (Phil. Mag. xxiv. p. 575, 1912), that between a large sphere and a small illuminated electrode placed at its centre, then an electron could escape if its total kinetic energy, and not necessarily that part of it due to motion in a particular direction, exceeded rE , and the relation (2) would be replaced by

$$\{E^2 - \beta x \sec \theta\}^{\frac{1}{2}} > rE.$$

Using this relation instead of (2), we find that the rate of emission of electrons is proportional to

$$\begin{aligned} & \frac{d}{\lambda} (1 - r^2) \\ &= \frac{d}{\lambda} \left(1 - \left(\frac{W + P}{E} \right)^2 \right) \quad (\alpha), \end{aligned}$$

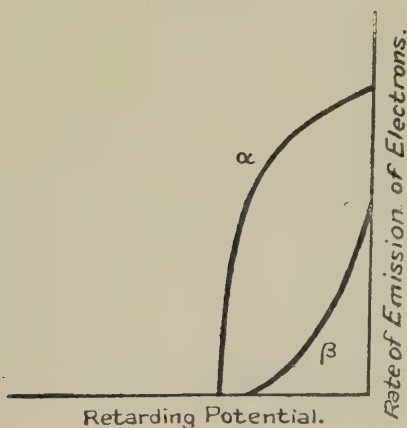
instead of, as in our case,

$$\frac{d}{\lambda} \left(1 - \frac{W+P}{E} \right) \quad (\beta).$$

The graph represented by α is also a parabola, but it is of the type shown in fig. 4 (α), while the graph for β is represented by fig. 4 (β).

With the relation α the slope of the graph vanishes when $r=0$ and is greatest when $r=1$, while with the graph β the slope vanishes when $r=1$ and is greatest when $r=0$.

Fig. 4.



If the radiation were heterogeneous the slope of the α -graph would vanish when $r=0$, though it would not necessarily be greatest at the place on the graph where emission vanished. For the β graph for heterogeneous radiation the slope would vanish when the emission vanished and would be greatest when $r=0$. The graphs in my experiments are always of the β type, and what I think is significant is that though in the majority of cases the graph cannot be represented by a single parabola, there are a few cases, one of which is the radiation given out by the glow next the anode in the discharge through pure oxygen, where the approximation to the parabolic form is very close. This is what we should expect if the radiation were in general heterogeneous, but there are special cases in which it is approximately homogeneous.

Experiments to determine the Distribution of Energy in the electrons emitted by the photoelectric effect of the radiation.

The arrangement used is shown in fig. 2. D is the disk connected with the electrometer by the insulated rod R; this rod is surrounded by a metal tube connected with the earth to shield off electrostatic effects from the disk and its connexions. In front of the disk and parallel to it is a sheet of wire gauze turned back at the ends as in the figure, so as to surround the disk with an equipotential surface. When the ends were not turned back I found the results depended to some extent on the distance between the plane of the gauze and that of the disk. I attribute this to some of the electrons escaping through the gap between the gauze and the disk without coming under the influence of the retarding potential. The wire gauze was connected with a battery of storage cells, and differences of potential ranging up to 400 volts could be established between the gauze and the disk; if the gauze were negative with respect to the disk the electric field tended to stop, if it were positive to promote the emission of electrons. The rates of emission of electrons for a series of potential differences were measured by finding the deflexion of the electrometer due to the exposure of the disk to the radiation for a fixed time. The readings with the same difference of potential between the gauze and the disk were fairly constant when the conditions were good, even when the radiation came from a discharge produced by an induction coil. To standardize the readings, the deflexion when there was no potential difference between the gauze and the disk was measured at frequent intervals.

When the coil was working well the deflexions of the electrometer were fairly constant with similar conditions. These investigations, however, brought to light a striking feature of the radiations produced by the discharge: the character of the radiation may change quite abruptly, sometimes without any appreciable change in the appearance of the discharge. I think these changes are due to gases coming off the walls of the tube or to incursions of mercury vapour; later on, experiments are described which show that when heavy gases are introduced into the tube radiations of much higher frequency are added to those already in the tube.

In order that the discharge should be able to pass through the tube the pressure must not be too low; in the great majority of these experiments the pressure was above

01 mm. of Hg, and was thus much higher than that occurring in recent experiments on photoelectric action.

In my experiments a considerable increase in the emission of electrons was produced by putting an accelerating potential on the gauze—*i. e.*, the emission was greater when the gauze was positive to the plate than when the gauze and plate were at the same potential.

Another effect frequently observed was that when the gauze was strongly negative to the plate, the plate not merely ceased to lose electrons when exposed to the radiation but slowly acquired a negative charge. The effect was small and soon showed saturation, *i. e.* the rate of increase of the negative charge soon becomes independent of the difference of potential between the gauze and the plate.

This effect might occur if the gas between the gauze and the plate were ionized by the radiation so that a current of negative electricity passed from the gauze to the plate; it would also occur if some of the radiation were reflected from the disk on to the wires of the gauze so that these gave out electrons by photoelectric action. There are, however, grave difficulties in accepting one or both of these explanations. If the effect were due to the ionization of the gas, then it would increase with the amount of gas surrounding the disk and exposed to the radiation. The apparatus was designed to make this as small as possible, and when the position of the gauze was altered so that the distance between it and the disk was increased and therewith the amount of ionizable gas, the negative effect diminished instead of increasing. Again, if it were due to the reflected radiation it ought to diminish if the surface of the metal in the wire gauze is diminished. I tried the effect of replacing one piece of gauze by another made of much finer wire and more open mesh, but I could not detect any diminution in the negative effect.

The experiments seem to me to indicate that there is at the surface of the disk a layer of ionized gas containing positive as well as negative ions, and that when the gauze is very strongly negative some of the positive ions are pulled out of this layer, so that the disk gets a negative charge. The existence of this retrograde current has to be taken into account in interpreting the graphs, for when the disk neither gains or loses a positive charge it does not necessarily follow that the flow of electrons from it has completely stopped; it may be that there is still a small flow from the disk which is just balanced by the retrograde current, so that E , the energy given to an electron by the light quantum, will be somewhat

greater than the value given by the equation

$$E = W + P,$$

where W is the retarding potential when the disk neither gains nor loses an electric charge.

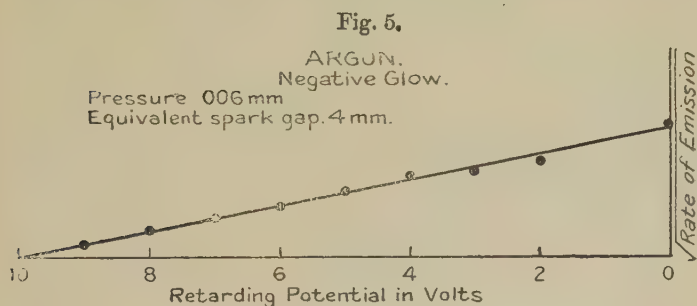
The retarding potential was got from a potentiometer consisting of 100 resistance coils placed in series. The electromotive force on the potentiometer was provided by a battery of small storage cells. To allow for possible variations in the induction coil, readings of the deflexion of the electrometer when there was no retarding potential were taken between those for the different retarding potentials. A convenient way of detecting changes in the character of the radiation is to apply by means of the potentiometer a retarding potential which reduces the flow of electricity to the disk to zero. When the coil is working well, it is possible to get so good a balance that there is not a deflexion of one division on the scale of the electrometer in several minutes. This balance often remained undisturbed when the pressure of the gas in the discharge-tube was altered and with it the potential difference between the electrodes, showing that the limiting radiation did not change appreciably with the physical conditions but was determined by the nature of the gas. If when it is in this state the liquid-air traps which have been used to take out impurities be removed, the balance will suddenly change and it will require a larger retarding potential to stop the flow of the electrons from the illuminated disk, showing that a radiation of a harder type has been introduced, probably arising from the heavier molecules liberated by the removal of the liquid air. This explanation is supported by the fact that the change in the retarding potential required to stop the emission is much more marked than the change in the rate of emission when no retarding potential is applied; this would be the case if a small quantity of radiation of a harder type were produced by some impurity in the gas.

Discussion of the Experiments.

A large number of experiments on the relation between R , the rate of emission from the illuminated copper disk, and W , the retarding potential, were made and the results analysed to find the nature of the radiation. In some cases examples of which are given below, the whole of the graph could be very approximately represented by a single parabola, so that when $\sqrt{R}$ was plotted against W the result was

a straight line. Examples of this are given in figs. 5, 6, and 7.

Fig. 5 is for the radiation from the negative glow in argon, the pressure was $\cdot 006$ mm., the discharge was produced by an induction coil and the equivalent spark-gap was 4 mm. It will be seen that the graph for $\sqrt{R}$ and W is very approximately a straight line and that the emission



vanishes when $W = 10$ volts; thus E , the quantum of energy in the radiation, will be given by

$E = 10 + P + a$ correction due to the retrograde current.

Taking W as 3.5 volts, this makes the quantum somewhat greater than 13.5 volts.

Fig. 6.

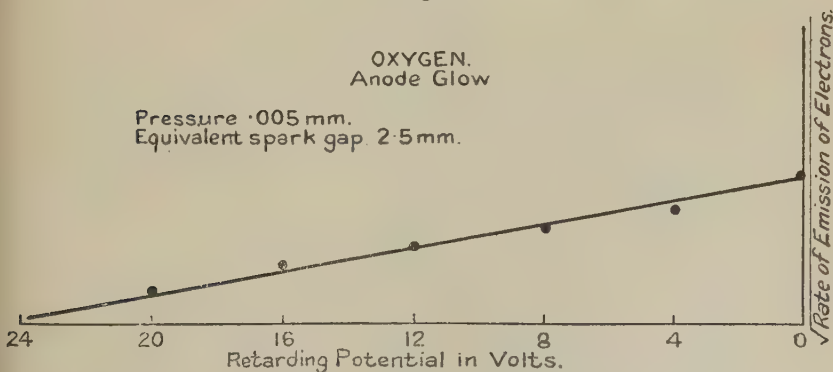


Fig. 6 is the graph for $\sqrt{R}$ and W for the radiation from the anode glow in oxygen at a pressure of $\cdot 005$ mm.; the discharge was produced by an induction coil and the equivalent spark-gap was 2.5 mm. Again the radiation is approxi-

mately homogeneous, and the emission vanishes when the retarding potential is 24 volts.

Fig. 7 is the graph for the negative glow in oxygen when the discharge was produced by a continuous-current dynamo; the potential difference was 400 volts and the current through the tube 2.6 milliamperes, the pressure was .045 mm.; the emission is stopped by a retarding potential of 12 volts, so that the quantum of radiation is considerably less than in the preceding case.

It is only, however, in exceptional cases that the graph for $\sqrt{R}$ and W is a straight line throughout the whole of its length; it much more frequently happens that the results for the higher retarding potentials are approximately on a straight line, while those for the smaller ones are far from the prolongation of this line.

Fig. 7.

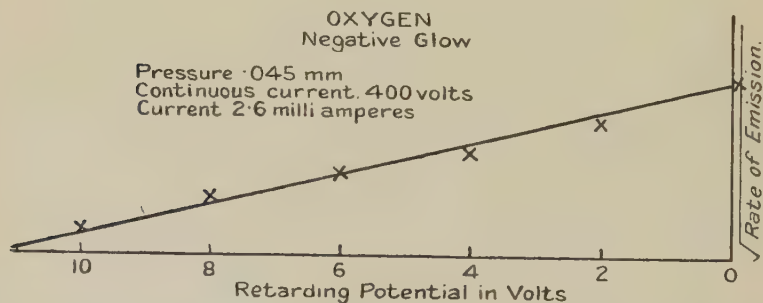


Fig. 8 is the graph representing the relation between R and W for the radiation from the negative glow in the discharge produced by an induction coil through hydrogen at the pressure of .01 mm. of mercury; the equivalent spark-gap was 4 mm. The unbroken line represents the observations, the dotted lines the two parabolas

$$y = \frac{26(10 - W)^2}{100}$$

$$\text{and } y = \frac{12(2 - W)^2}{4};$$

the sum of the ordinates of these is not distinguishable from the graph on the scale of the diagram. We conclude from this that the radiation was concentrated in two types, one having the energy quantum equal to $10 + P$, and the other a radiation of a much softer type with the energy quantum equal to $2 + P$.

Fig. 8.

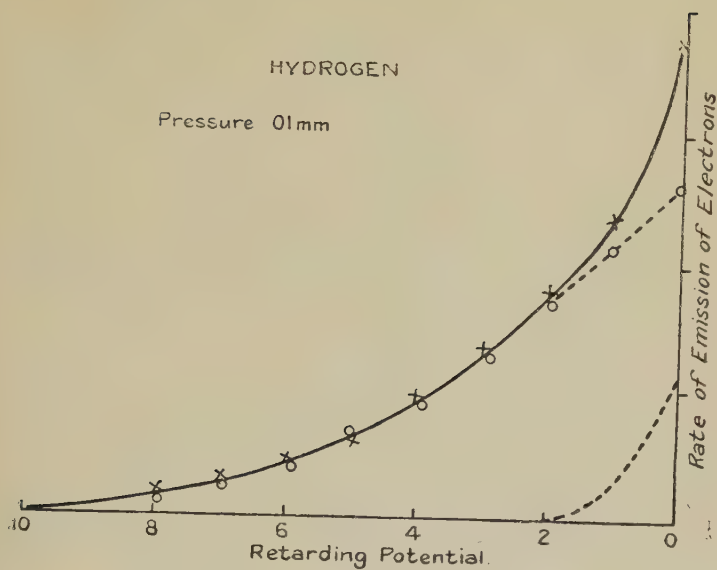


Fig. 9.

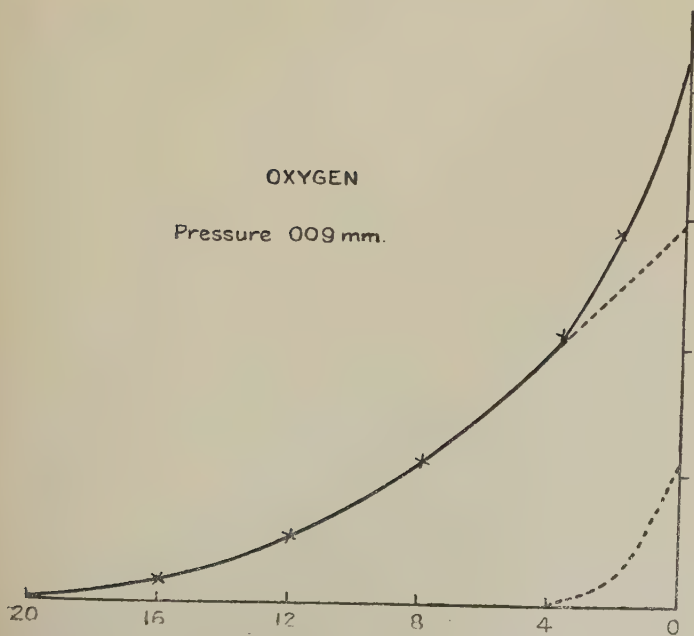


Fig. 9 is the graph representing the radiation from the

negative glow in the discharge through oxygen at the pressure .009 mm. of mercury produced by a large induction coil; the equivalent spark-gap was 4.0 mm.

The graph can be represented by the superposition of the two parabolas

$$R = \frac{39}{256} (20 - W)^2,$$

$$R = \frac{25}{16} (4 - W)^2.$$

This implies that the radiation consists in the main of two constituents, one having for energy quantum $20 + P$ volts, and the other $4 + P$ volts.

The graphs for the radiation from the negative and anode glows were obtained by using a piece of gauze placed in front of the window through which the radiation passed on its way to the disk connected with the electrometer as the cathode or anode for the electric discharge. With this arrangement the deflexions of the electrometer were very large, and capacities sometimes as large as .1 microfarad had to be connected to the electrometer to reduce the deflexion to measurable dimensions. The illuminated disk was in this case receiving radiations of the same kind as those which fall on the metal surface of the cathode or anode of the discharge-tube, and as the disk emits copious streams of electrons, it follows that both the anode and cathode in the discharge-tube receive radiation which induces a copious emission of electrons. This emission at the cathode gives rise to the high-speed cathode-rays; while the emission at the anode proceeds until the electrons accumulate in front of the anode in sufficient density to produce a retarding potential sufficient to stop the flow of the electrons. This potential must be equal to that found in the experiments we have just described. The existence of an anode fall of potential was proved many years ago by Skinner, and the magnitude of it was found to be in the neighbourhood of about 20 volts with variations of a few volts depending on the gas in the tube and the nature of the anode. It is thus of the same order of magnitude as the retarding potential necessary to stop the flow of electrons measured in the preceding experiments.

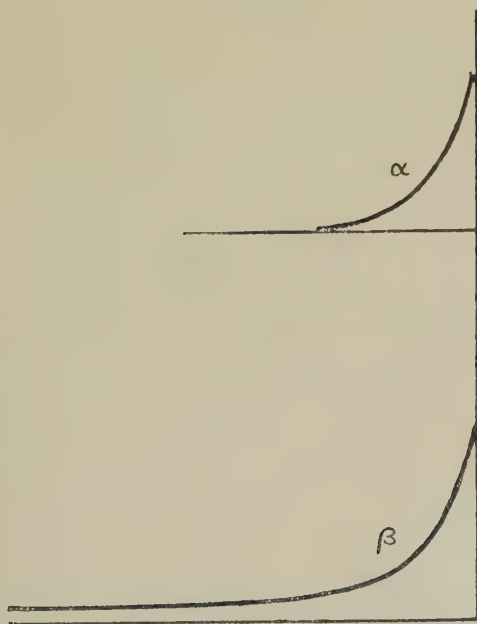
To test whether the effect observed in these experiments was wholly due to radiation coming from the tube and not in part due to uncharged atoms or molecules in an excited state making their way through the screen and then giving out radiation, the disk connected with the electrometer was placed in a side tube so as to be out of the way of radiation

from the tube, and by means of a pump a constant stream of gas was drawn from the discharge-tube past the disk : there was, however, no deflexion of the electrometer.

Radiation produced by the passage of Cathode and Positive Rays through Gases.

I have investigated the radiation produced when cathode and positive rays pass through hydrogen, helium, and argon. When the pressure is not lower than .01 mm. the graphs for the radiation from the cathode and positive rays are not very different; they all showed that the emission of electrons was stopped by retarding potentials which rarely exceeded 12 volts. The analysis of the graphs showed that the radiation

Fig. 10.



was by no means homogeneous. The radiation produced when the positive rays struck against metals gave graphs similar to those due to the radiation produced by the passage of positive rays through the gas. At very low pressures when the potential difference between the anode and cathode is large, there is a distinct difference between the graphs for the radiations from the positive and cathode rays. The graphs for the positive rays are similar to those at the higher pressures and are of the type shown in fig. 10 α , while the

graph for the radiation from the cathode rays is of the type of fig. 10 β .

In both cases we have on the application of a small retarding potential a rapid fall in the rate of emission of electrons. With cathode rays, however, this initial rapid fall is succeeded by a stage where the deflexion diminishes only slowly with the retarding potential, and there may be an appreciable emission with a retarding potential as great as 100 volts. With the radiation from the positive rays we have only the stage represented by the rapid fall at the beginning, the emission vanishes when the retarding potential is only a few volts. This indicates that in the radiation from the cathode rays we have a mixture of soft radiation with quanta represented by a few volts with much harder radiation whose quanta may be comparable with a hundred volts. With the positive rays the radiation is all of the softer type.

The production of ionizing radiation by positive rays passing through a gas or striking against a solid has an important bearing on the question of whether or not positive particles ionize by collision. Ionization by positive particles has been observed and measured by Pavlow (Proc. Roy. Soc. A, xc. p. 898, 1914) and others, and has been interpreted as a proof that such particles as well as electrons produce ions by collision. There are, as I have pointed out, very serious theoretical objections to this view, and such results as have been obtained may be explained as due to the radiation emitted by the particles. This radiation will give rise to the emission of electrons from the molecules of the gas and from the surfaces of solids in the discharge-tube, and it is to this and not to direct collisions that we ascribe the ionization observed by Pavlow.

There is still very much that is obscure about the ionization due to positive rays. Seeliger (*Physik. Zeit.* xii. p. 839, 1912) has made quantitative experiments on the subject, and these indicate that the total number of ions produced by a positive ray is but small, very far below the number which would exhaust the kinetic energy of the ray; he found that the number does not vary much either with the speed of the ray or with the pressure of the gas. These results would follow if the ionization were due not to the energy of translation of the particle but to energy internal to the particle, such as might be represented by supposing the particle to contain a limited number of undischarged quanta of radiation, and that it is these, and not the translational energy of the particle, which produce the ionization.

The Electrodeless Ring Discharge.

A copious and convenient source of radiation of the type we are studying is supplied by the electrodeless ring discharge.

When a solenoid is placed in the circuit connecting the outer coatings of two Leyden jars, whose inside coatings are connected with the terminals A, B of an induction coil, when sparks pass between these terminals electrical oscillations are excited and the solenoid is traversed by rapidly alternating currents. If a glass vessel containing gas at a low pressure is placed inside the solenoid, the rapidly alternating currents in the solenoid will by electromagnetic induction produce in the vessel closed lines of electromotive force, and these when the pressure of the gas inside is low produce a ring discharge which is often exceedingly bright. The study of the radiation given out by this discharge has led to some interesting results.

The arrangement adopted was as follows: the solenoid was placed over the tube C in fig. 1 so that the ring discharge is well in sight of the disk used to test the photo-electric effect due to the radiation. Measurements were made on the rate of emission under different retarding potentials. The results seemed to depend to a great extent upon the purity of the gas. With very pure helium or hydrogen a retarding potential of about 12 volts was sufficient to stop the emission of electrons from the illuminated disk, while for oxygen a potential difference of about 24 volts was required. The magnitude of the limiting potential did not seem to vary with the pressure of the gas or the frequency of the discharge. The analysis of the graphs showed that the radiation was not homogeneous. Not infrequently, however, abrupt changes took place in the retarding potential required to stop the emission of electrons, and instead of 12 volts being sufficient, in some cases more than 100 volts were required.

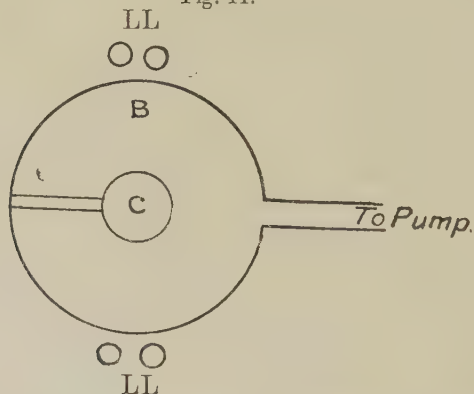
These changes sometimes occurred spontaneously; they could generally be brought about by removing the liquid-air trap used to free the gas from mercury vapour. Though the change in the limiting potentials may be great, there is not a correspondingly large change in the rate of emission of the electrons when there is no retarding potential. It would seem as if the effect were due to the presence of an impurity which emits a much harder type of radiation than that coming from the pure gas.

Radiation from dark electric discharge.

The luminous rings characteristic of the electrodeless discharge appear only when the pressure of the gas is within somewhat narrow limits; but even at pressures lower than those where the luminous radiation appears the electrometer gives large deflexions showing the existence of radiation of smaller wave-lengths than those of visible light. The analysis of this radiation by the method of the retarding potential shows that it is mainly in the region of the radiation which has a quantum of the order of the ionizing potential of the gas.

The following experiment supplies direct evidence of the existence of currents through the gas even when there is no luminosity.

Fig. 11.



C is a bulb containing gas at a pressure at which the luminous discharge is very bright; it is placed inside another bulb B connected with a pump. The coils LL for producing the electrodeless discharge are placed outside B. When the gas in B is at atmospheric pressure there is a bright ring discharge in C; but when the pressure is reduced so that the ring discharge appears in B, that in C disappears. The gas in B is a conductor of electricity and the currents induced in it shield off from C the effects due to the currents through the coils LL. When the pressure in B is reduced so that the vacuum in B is a very high one, the bright ring discharge appears again in C: the induced currents through B are not now sufficient to shield off the effects of the primary current. There is, however, a considerable range of pressure in which, though there is no visible discharge in B, that in C is stopped; showing that there are sufficient

currents passing through B without exciting visible luminosity, to shield off the effects of the primary currents. As there would be but little shielding unless the currents passing through the gas were comparable with those which pass through the coil, this experiment shows that large currents may pass through the gas under certain conditions without exciting visible luminosity, though, as we have seen, they do excite radiation of smaller wave-length.

The following calculation shows that when the effect of the primary coil is shielded by the currents in the rarefied gas, a large number of electrons must be present in the gas.

Let us suppose that the coil is a long straight solenoid ; consider the free motion of an electron in an exhausted tube coaxial with the solenoid. Let r, θ, z be the cylindrical co-ordinates of an electron, z being measured parallel to the axis. Then, if H is the magnetic force due to the currents in the solenoid and gas, the electric force at a point distance r from the axis is $\frac{r}{2} \frac{dH}{dt}$ and is tangential. Hence the equations of motion of a free electron are

$$m \frac{1}{r} \frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) = \left\{ \frac{1}{2} r \frac{dH}{dt} + \frac{H}{dt} \frac{dr}{dt} \right\} e, \quad . \quad . \quad (1)$$

$$m \left(\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 \right) = -H e r \frac{d\theta}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where m is the mass, and e the charge on an electron.

The first of these may be written in the form

$$\frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) = \frac{e}{2m} \frac{d}{dt} (H r^2),$$

$$r^2 \frac{d\theta}{dt} = \frac{e}{2m} \cdot H r^2 + C;$$

if $d\theta/dt$ and H both vanish when $t=0$,

$$r^2 \frac{d\theta}{dt} = \frac{e}{2m} H r^2$$

$$\text{or} \quad \frac{d\theta}{dt} = \frac{e}{2m} \cdot H.$$

The velocity of the electron at right angles to r is thus

$$\frac{e}{2m} r H;$$

and if ρ is the density of the electrons, the current per unit length of the gas

$$\frac{e^2}{2m} \int_0^a H \rho r dr,$$

where a is the radius of the tube. If N is the number of electrons contained between two planes at right angles to the axis of the tube and unit distance apart,

$$\int_0^a \rho \cdot r \cdot dr = \frac{N}{2\pi};$$

thus the currents through the gas are less than

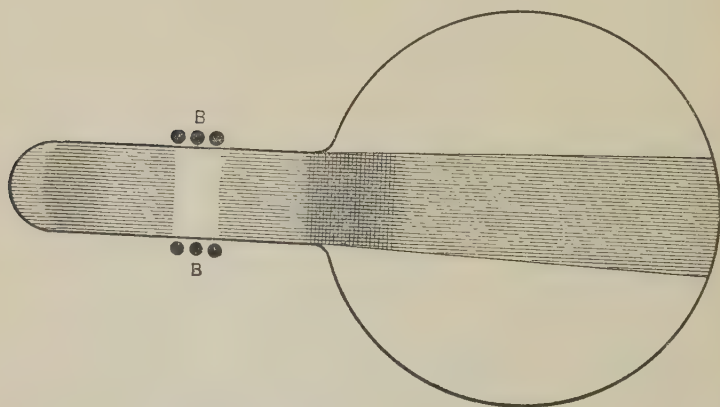
$$\frac{e^2 N H_0}{4\pi m}.$$

where H_0 is the value of H when $r=a$, if c is the current through unit length of the solenoid,

$$H_0 = 4\pi c;$$

hence the current through the gas is less than Ne^2/m times the current through the coil. If the current through the gas is to neutralize the effect of that through the coils,

Fig. 12.

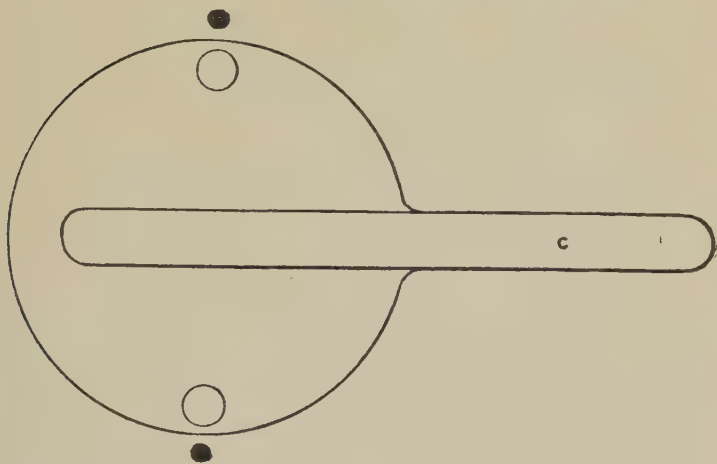


the magnitude of the gaseous current must not be less than that through the coils, hence Ne^2/m must not be less than unity, since e^2/m is 2.8×10^{-13} , N must not be less than 3.6×10^{12} .

The radiation produced by the electrodeless ring discharge is so intense that it is easy to demonstrate its existence by experiments which are suitable for the lecture-room.

One of these is the following. The vessel containing the gas is shaped as in fig. 12. It is a large spherical bulb with a neck about 4 cm. in diameter at one end. The coil for producing the electrodeless discharge is placed round the neck at B, and the bright ring discharge occurs here. Adjoining the ring there is bright luminosity : if the gas is hydrogen, this is a light pink in the layers adjacent to the ring and shows both the Balmer and the second spectrum of hydrogen ; this is succeeded by a brilliant red layer showing only the Balmer lines, the boundaries of this layer are fairly well defined. In oxygen the luminosity in the region adjacent to the ring is a brilliant blue. This very bright

Fig. 13.



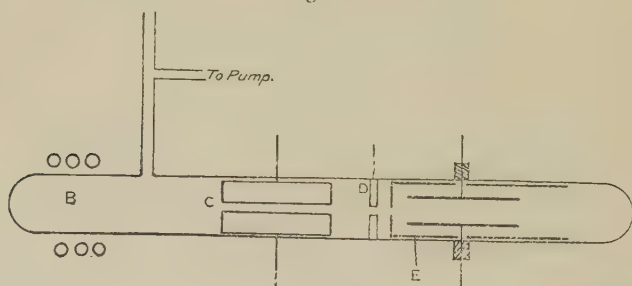
luminosity only extends a few centimetres from the ring ; it is succeeded by fainter luminosity not of the same colour, which can be traced as a luminous cone extending right through the bulb. The glass of the bulb phosphoresces over the area covered by the cone ; this phosphorescence is not of the same colour as that due to cathode rays : another proof that it is not produced by these rays is that the distribution of the phosphorescence is not affected when a magnet is brought near it. The existence of this phosphorescence can be shown by the experiment, fig. 13, where C is a glass tube covered with willemite placed along a diameter of the large bulb in which the ring discharge is produced in a plane at right angles to the tube ; when the ring discharge passes

the tube phosphoresces and the distribution of the phosphorescence is not affected by a magnet.

The ionization produced by the radiation can be shown by the experiment represented in fig. 14.

The ring discharge is produced at B. C is the electrostatic filter, consisting of two halves of a brass cylindrical rod, insulated from each other and connected to the terminals of a battery of a large number of small storage cells. D is a brass plug fitting closely into the glass tube, a slit is cut at the centre of this plug so as to be parallel to the space between the two halves of the electrostatic filter. This plug is kept permanently connected with the earth, its object is to shield off any effects due to the high potential of the filter ;

Fig. 14.



beyond the plug are two parallel brass plates, so far apart that no radiation passing through the plug can strike against them ; one of these plates is connected with the earth, the other to the gold leaves of an electroscope. When the ring discharge is passing at B, the electroscope leaks whether the charge in it is positive or negative, showing that the gas between the plates has been made conductive by the radiation.

SUMMARY.

The paper contains an account of experiments on the character of the radiation produced when electric currents pass through gas at a low pressure. The method adopted was to let the radiation fall on a disk of metal and measure the variation in the rate of emission of electrons due to the photoelectric effect when the emission was retarded by an electric field tending to stop the escape of electrons. The theory of the variation of the rate of emission with the strength of the field is worked out, and methods are given for determining from the graph representing the relation

between rate of emission and the potential difference in the retarding field the spectrum of the radiation.

The radiation produced by the passage of cathode and positive rays through the gas, that from the negative and anode glows in hydrogen, oxygen, helium, and argon at different pressures are discussed. It is found that the frequencies of by far the greater part of the radiation are comparable with those corresponding to quanta of the order of the ionizing and resonance potentials of the gas, in the case of the radiation due to the cathode rays these radiations are mixed with others of a higher frequency.

In a few cases the radiation was found to be fairly homogeneous, but in general it is a mixture of radiation having a frequency comparable with that of the ionizing radiation with other radiation of a lower frequency.

The electrodeless ring discharge is found to be a very copious and convenient source of radiation of this type, and various lecture-room experiments are described for demonstrating the existence and properties of the radiation.

I have much pleasure in thanking Mr. E. Everett and Mr. Morley for their assistance in making these experiments.

LX. *Electric Double Refraction in Colloids.*

By YNGVE BJÖRNSTÅHL *.

(From the Laboratory of Physical Chemistry, Upsala.)

[Plate XIII.]

BY accidental double refraction is meant the phenomenon that a medium, during the action of external agents, assumes optical properties similar to those of a uniaxial crystal. Thus the behaviour is not characteristic for the substance *per se* in its non-excited state, but is produced, for example, by a magnetic or an electric field.

The magnetic double refraction in liquids was first studied by A. Cotton and H. Monton †. In a previous communication the author has given an account of the magnetic double refraction in certain colloids ‡. Analogous to the phenomenon in a magnetic field a double refraction also appears in an electric field. This action has been subjected to detailed investigations and is often called the electric Kerr effect.

* Communicated by the Author.

† *C. R.* cxlv. p. 229 (1907).

‡ *Phil. Mag.* xlii. p. 352 (1921).

after its discoverer, J. Kerr*. Plane polarized light is passed through a medium in a direction perpendicular to the lines of force. The azimuth of the plane of polarization should then form an angle of 45° with the lines of force. The emergent beam is elliptically polarized. The vibrations parallel to and at right angles to the lines of force display a difference in phase and eventually a change of the amplitudes, the two vibrations being absorbed to a different extent. There are two circumstances that characterize the electric double refraction in ordinary liquids: (1) the retardation is proportional to the square of the intensity of the field, and (2) no dichroism is found. The exception recorded by Meslin†, viz. dichroism in a solution of potassium dichromate in carbon disulphide, may be disregarded since the solution represents a coarse suspension. The time of disappearance of the double refraction in ordinary liquids, *i. e.* the time of relaxation, is very short; according to Abraham and Lemoine‡ less than 10^{-8} sec.

With reference to colloidal solutions, it is to be noted that de Metz§ in his investigations of the Kerr effect in conducting liquids made certain experiments with a three-per-cent. gelatine-water solution. This system at ordinary room temperature is a gel, and consequently the nature of the double refraction is dubious. It is not until 1915 that we can record any experiments in the true sense. That the study of the electric double refraction was not begun until so late a period is probably due to the fact that the colloidal systems as a whole were investigated at a comparatively late date; this especially concerns the colloids in dispersion media other than water. Dieselhorst, H. Freundlich, and W. Leonardt||, while studying vanadium pentoxide sols, found that the sol showed double refraction in an electric field, or in the words of the authors: "auch unter dem Einfluss des elektrischen Stromes tritt unter geeigneten Bedingungen Aufhellung zwischen gekreuzten Nicols auf"¶. The present writer, however, was the first to make any measurements on such sols. The experiments were continued later in collaboration with C. Bergholm**. Some measurements on gold sols were also made.

* Phil. Mag. [4] l. p. 337 (1875).

† C. R. cxxxvi. p. 888 (1903).

‡ C. R. cxxix. p. 206 (1899).

§ Journ. de la Soc. Phys.-Chem. Russe, xxxiv. p. 505 (1902).

|| 'Elster-Geitel-Festschrift,' p. 476. Vieweg & Sohn, Braunschweig, 1915.

¶ L. c. p. 463.

** Phys. Z. xxi. p. 137 (1920).

Although this paper is devoted to colloidal solutions in the narrow meaning of the expression, the experiments with coarse suspensions made by Meslin * should be cited in this short historical survey. He observed "dichroism" in a suspension of helianthine crystals in carbon disulphide. The experiments were continued by Chaudier †, who studied the dichroism with the aid of a Soleil polariscope, and the double refraction with a Bravais double-plate. He investigated, for example, such systems as powdered mica suspended in benzene, and gypsum in benzene ‡. The experimental methods in themselves show only the sign of the double refraction and the direction of the maximum absorption. The investigations of St. Procopiu § on suspensions of various mineral powders, such as calc-spar and zircon, follow the same line. The double refraction was measured with a half-shade analyser, not described in his paper. A positive double refraction is ascribed to the difference between the ordinary and the extraordinary refractive index of the crystals; a negative one to the hypothesis that the particles arrange themselves as strings in the field.

Measurements.

A large number of colloids are included in the present investigations. Among these may be mentioned the metal sols of gold, silver, copper, platinum, mercury, molybdenum, tungsten, bismuth, antimony, iron, nickel, and titanium. In addition, however, experiments have been made with sols of non-metallic disperse phase, such as carbon, sulphur, antimony trisulphide, arsenic trisulphide, vanadium pentoxide, starch and gelatine, and many dyestuffs. As a general rule it may be stated that the first of the two above-mentioned groups is characterized by an electric double refraction of negative sign. As to the non-metallic colloids, on the other hand, a rule cannot be given. It cannot be said, however, that the electric double refraction is a property characteristic of all sols. It is possible to trace an effect only at a certain degree of dispersity.

With regard to protected colloids, it may be mentioned in

* *C. R.* cxxxvi. p. 930 (1903).

† *C. R.* cxxxvii. p. 248 (1903).

‡ *Ann. de Chimie*, xv. p. 67 (1908).

§ *C. R.* clxxii. p. 1172 (1921). Later on he collected his measurements in the work: 'Sur la biréfringence électrique et magnétique des suspensions,' Thèses, Paris, 1924, in which he also describes some experiments with metal suspensions.

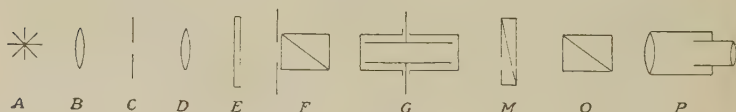
passing that they show less double refraction than do unprotected ones. This applies to Au, Pt, Bi, Fe, Mo, W, Ag, Cu, Ni, C, Sb, Ti, Sb_2S_3 , As_2S_3 , Fe_2O_3 . A number of alcohols also have been examined.

An account is given in the following pages of the electric double refraction in mercury, gold, and sulphur hydrosols.

Apparatus.

Several different experimental arrangements were used, one of which is shown in fig. 1. The lens *B* throws an image of the arc *A* on the rectangular slit *C*, and this image is projected on the objective of the telescope *P* by the lens *D*. The light is passed through the monochromatic filter *E*, a polarizing Thomson-Glan prism *F*, the trough *G*, the compensator *M*, the analysing prism *O*, and, finally, through the telescope *P*. The compensator was of the type designed

Fig. 1.



by D. B. Brace* and afterwards employed by many scientists. The arrangement consists of two plates of mica. The first, the compensator proper, covers the whole field of view and is mounted on a graduated circle, the rotation of which can be read. The half shade, or the sensitive strip, consists of a thin sheet of mica inserted in an azimuth of 45° and covering only the centre of the field of vision. This sheet is mounted in balsam between carefully selected cover-glasses free from double refraction. The sensitive strip can be placed either before or after the compensator. The first method is the most frequently used, and has also been used by the author. The principal sections of the polarizing prisms were crossed, and formed an angle of 45° with the lines of force. The telescope was focussed on the sensitive strip, the angle between the principal axis of the latter and that of the prism being 45° . The compensator was turned so as to obtain a uniformly illuminated field of view, the electric field was applied, and the compensator set for a match again.

The theory of this compensator has been treated by L. B.

* Phil. Mag. 6 v. p. 161 (1903).

Tuckerman*, L. Chaumont†, and C. Bergholm‡. If ψ is the angle between the principal planes of the analyser and of the compensator, and if δ is the angular retardation of the compensator, we obtain

$$\tan\left(\Delta + \frac{\epsilon}{2}\right) = \frac{\sin 2\psi \sin \delta}{1 - 2 \sin^2 2\psi \sin^2 \frac{\delta}{2}}, \quad \dots \quad (1)$$

where Δ is the unknown phase difference, and ϵ is the phase difference of the sensitive strip. If $\Delta = 0$, we obtain

$$\tan \frac{\epsilon}{2} = \frac{\sin 2\psi_0 \sin \delta}{1 - 2 \sin^2 2\psi_0 \sin^2 \frac{\delta}{2}}, \quad \dots \quad (2)$$

where ψ_0 represents in this case the angle between the compensator and analyser. Subtracting (2) from (1), we have

$$\frac{\tan \Delta}{\left(1 - \tan \Delta \tan \frac{\epsilon}{2}\right) \cos \frac{\epsilon}{2}} = \frac{2 \sin \delta \cos (\psi + \psi_0) \sin (\psi - \psi_0) \left[1 - 2 \sin^2 \frac{\delta}{2} \sin 2\psi \sin 2\psi_0\right]}{\left(1 - 2 \sin^2 2\psi \sin^2 \frac{\delta}{2}\right) \left(1 - 2 \sin^2 2\psi_0 \sin^2 \frac{\delta}{2}\right)}.$$

C. Bergholm§ has shown that the equation (1) is valid independent of the double refraction, being united with the amplitude effect; in other words, if the axis of the ellipse of the emergent light has an azimuth differing from 45° . If suitable approximations are made, we obtain

$$\tan \Delta = 2 \sin \delta \cos (\psi + \psi_0) \sin (\psi - \psi_0).$$

Bergholm has also indicated the range over which this approximate formula can be used. If we put $\psi - \psi_0 = \theta$, the rotation of the compensator, the expression may be written

$$\tan \Delta = 2 \sin \delta \sin \theta \cos (2\psi_0 \pm \theta).$$

In order to analyse the elliptically polarized light emerging from the tube G, it is sufficient to measure first the phase

* Cf. University Studies, published by the University of Nebraska, ix. No. 2.

† Thèses, Paris, 1914.

‡ Diss., Upsala, 1915.

§ L. c.

difference between the components parallel and perpendicular to the lines of force, then the azimuth of the major axis of the ellipse, the elements of which are defined by this with regard to form and position.

In order to determine the azimuth of the ellipse, a quarter-wave plate was inserted between the tube G and the compensator (*cf.* fig. 1). The plate is rotated to obtain linear polarized light, which is tested with the Brace apparatus. The azimuth of the quarter-wave plate is read. This arrangement is described by Cotton and Mouton*, who employed it for the study of dichroic circular polarization, by M. G. Bruhat†, and independently by Bergholm‡, who has given full particulars about the method. If the liquid is considered to be a uniaxial dichroic crystal, with the axis along the lines of force, then the absorptions of the parallel and of the perpendicular components are different. Calling the rotation of the quarter-wave plate ϕ and the specially determined phase difference Δ , we can derive the ratio ρ of the parallel amplitude to the perpendicular one, $\rho = \frac{a_{\parallel}}{a_{\perp}}$ from the equation

$$\frac{1 - \rho^2}{2\rho} = \tan 2\phi \cos \Delta.$$

The usual precautions were taken in order to eliminate the error arising from the fact that the quarter-wave plate did not show a phase difference of exactly $\pi/2$. The quarter-wave plate is turned through an angle of 90° and a new reading is taken. The retardation of the plate of mica used as a compensator was determined by the aid of a plate of mica with a retardation amounting to nearly $\lambda/4$. The phase difference of these " $\lambda/4$ " plates was determined using a Babinet compensator. The constants of the plate of mica used as compensator are recorded in Table I.

TABLE I.
Constants of the compensator.

λ , (A.U.)	δ .	$2\psi_0$.
7000	$7^\circ 2'$	
6200	$7^\circ 33'$	$5^\circ 6'$
5900	$7^\circ 57'$	
5460	$8^\circ 33'$	$4^\circ 55'$
4360	$10^\circ 24'$	$4^\circ 55'$

* *Journal de Phys.* (5) i, p. 8 (1911).

† *C. R.* cliii. p. 248 (1911).

‡ *L. c.*

In order to define the sign of the double refraction, the medium in the field is regarded as a uniaxial crystal the axis of which is parallel to the lines of force.

The sign of the double refraction is considered as positive when the refractive index n_e for the ray which is polarized in a plane at right angles to the principal section in the crystal imagined (*i. e.* at right angles to the line of force) is greater than the refractive index n_0 for the ray which is polarized in the principal section. Thus, for a positive medium, $n_e > n_0$; for a negative one, $n_0 > n_e$. In the first case the more retarded vibration is propagated in the principal section, whilst in the second it is propagated in the section at right angles.

In some experiments the monochromatic filter was replaced by a monochromatic illuminator.

With regard to the experimental methods, it must be observed that relative measurements, *i. e.* comparison of the double refraction for a colloid and a normal substance, are meaningless on account of the double refraction not being quadratically dependent on the intensity of the field. Otherwise, in the question of the liquids here treated, all of which are conducting to a certain degree, the relative method of Des Coudres* would have been particularly suitable. When using this method it is unnecessary to know the voltage. High-frequency voltage of unknown wave-shape can be used.

For an absolute determination it is necessary to determine the voltage between the plates of the condenser. If such a determination is to have any meaning, the shape of the voltage curve must be known. Direct pressure cannot be used on account of electrolysis. An alternating electromotive force giving a sine-wave must be employed. Further, it is necessary that the frequency be as high as possible. Experiments on the decomposition of very dilute solutions of electrolytes showed an enormous decrease of the electrolysis when the frequency was increased from 200 to 1200 cycles per second. The voltage was obtained from a high-frequency alternator constructed by Hartmann and Braun, Frankfurt am Main. The alternator is supplied with a 48-pole rotor, which is fed by direct current from a storage battery. When the number of revolutions per minute is 3000, alternating current of the frequency of 1200 cycles per second is generated. The alternator is supplied with a distance tachometer of Hartmann and Braun's construction,

* *Verh. Ges. Deutsch. Naturforsch. u. Ärzte*, 1893 ii. p. 67.

so that it is possible to read the frequency at the laboratory. The machine is built with special regard to its giving an electromotive force wave of sine shape. The electric double refraction is dependent on the frequency. One of the first tasks was to investigate to what extent the voltage wave supplied by the machine was of sine shape.

If $f(t)$ is the electromotive force wave of the machine, then by Fourier's theorem we have

$$f(t) = \sum a_n \sin n \omega t + \sum b_n \cos n \omega t = \sum \sqrt{a_n^2 + b_n^2} \sin (n \omega t + \phi_n)$$

$$\tan \phi_n = \frac{b_n}{a_n}.$$

In order to find $f(t)$ we must determine the amplitudes $\sqrt{a_n^2 + b_n^2}$ and their time-lags ϕ_n . In order to measure the amplitudes the method first devised by Pupin* was employed. The potential difference, the wave of which is to be analysed, is applied to the terminals of a circuit consisting of a condenser in series with a coreless choke coil. An electrostatic voltmeter is placed across the condenser. The inductance is varied continuously and the voltmeter reading at resonance is noted. In this way it is possible to determine the amplitudes of the various harmonics.

With light load the amplitude of the third harmonic reached a value of 15 per cent. of the amplitude of the first harmonic. The other harmonics were small and could hardly be traced.

In order to eliminate the higher harmonics, a self-inductance and a condenser were connected in series and the potential difference at the terminals of the condenser was used. The arrangement can be considered as a potential divider. At the terminals of the condenser a considerably smaller fraction of the voltage corresponding to the higher harmonics appears than of the voltage corresponding to the first harmonic, answering to the proportion between the effective resistance of the capacity and that of the self-inductance. This proportion varies with the frequency. For the first harmonic the proportion is $1/LC\omega^2$; for the n th one it has the value $1/LCn^2\omega^2$, where L is the coefficient of the self-inductance, C the capacity of the condenser, and ω is 2π times the frequency.

For the proportion between the effective voltage across the condenser of the n th harmonic and that of the first

* Journ. of. Science, B, xlv. p. 325; B, xlviii. p. 379.

harmonic, we have the expression

$$\frac{a_n \sqrt{R + \left(L\omega - \frac{1}{C\omega}\right)^2}}{na_1 \sqrt{R + \left(Ln\omega - \frac{1}{nC\omega}\right)^2}}.$$

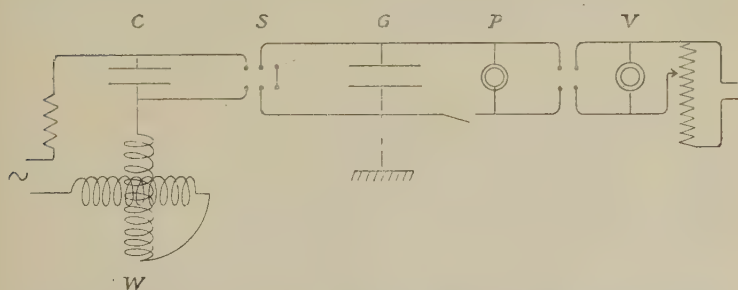
This expression will be a minimum when $\frac{1}{L\omega} = C\omega$.

The voltage was varied by changing the intensity of the current in the rotor, partly by means of an ohmic resistance, which served as a potentiometer.

The capacity consisted of a mica condenser of 1.0 microfarad and the self-inductance of a self-inductometer. The alternator was regulated to give a frequency of 1200 cycles per second, and the inductometer was then adjusted for resonance.

In order to determine the voltage between the plates of the cell, an alternating voltmeter, a dynamometer instrument from Siemens & Halske, was used first. As it was intended for a frequency of about 50 cycles per second, it was graduated with the aid of a quadrant electrometer for

Fig. 2.



the frequency employed, namely 1200 cycles per second. For the measurements the precautions proposed by Orlich* were observed. The quadrant electrometer in turn was compared with a Weston normal cell by means of a potentiometer.

Some experiments were made using a Bjerknes-Ebert† electrometer. In most of the measurements a hot-wire voltmeter made by Hartmann & Braun was employed. This was frequently compared with a precision voltmeter manufactured by Siemens & Halske, Berlin. The latter in turn was compared with a Weston normal cell by means of a compensation method.

A diagram of the electrical arrangement is given in fig. 2,

* *Z. f. Instr. K.* 1903, p. 97.

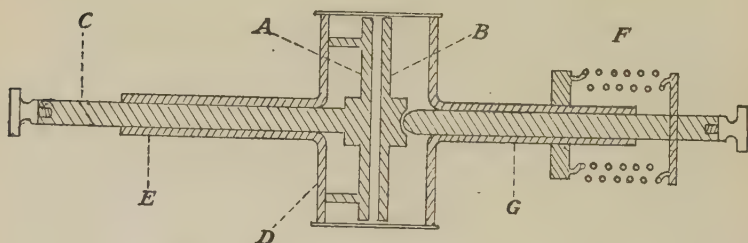
† K. Bjerknes, *Wied. Ann.* xlviii. p. 594 (1893).

where *G* is the trough, *C* the condenser, *W* the self-inductance, *S* a switch, *P* the voltmeter, and *V* a checking device for the voltmeter.

The Trough.

Through repeated experiments certain colloids were found to be less stable in metallic vessels. Hence it was necessary to use Jena normal glass as much as possible for the troughs employed in the experiments. This material also facilitates a more satisfactory cleaning of the trough. The condenser plates themselves naturally must be of metal. To reduce to a minimum the metallic surface which comes in contact with the liquid, experiments were made with glass plates plated with silver and then gilded on one side. The attempt failed because common soda glass was used. The idea was discarded at the time, because glass plates of less soluble glass could not conveniently be obtained within a reasonable

Fig. 3.



period. Instead, condenser plates of copper covered with thick gilding were made. The opposite surfaces were ground to a plane.

Fig. 3 shows the appearance of one of the troughs in a horizontal section (*cf.* also Pl. XIII.). The plates of metal *A* and *B* are enclosed in the glass tube *D*. The plate *A* is fixed to the cylindrical rod *C*, which is movable, with some play, in the side tube *E*.

The plates are kept apart by four small plates of glass inserted between them. The plate *B* is pressed against the plate *A* by the rod *G* and the spring attachment *F*. It is evident from Pl. XIII. that the trough is supplied with tubes for filling and emptying, together with a tube for the thermometer. On account of the instability of the sols the filling must be repeated for every reading. A convenient arrangement for this was therefore necessary. The sol is contained in a glass flask and is pressed into the trough by compressed nitrogen.

It was very difficult to obtain electrodes free from electrolytes. The galvanically gilded electrodes in particular seemed to have adsorbed large quantities of electrolytes. Only after repeated washings with distilled water, while the condenser plates were subjected to electrical discharges, was it possible to remove the electrolyte.

The distance between the plates is determined by the thickness of the glass plates inserted. This was measured with a micrometer screw gauge, which in turn was checked against Johansson gauges.

Correction of the Length of the Condenser.

The Kerr constant B is defined by the expression

$$\Delta = 2\pi B l E^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

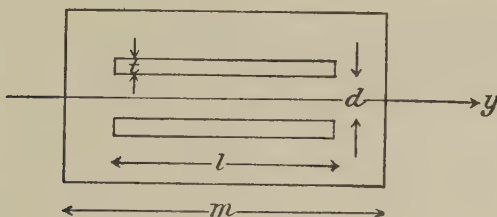
where Δ is the phase difference between the vibration parallel to the lines of force and that at right angles.

l is the length of the condenser (cm.).

E is the intensity of the field (electrostatic units).

At the edge of the condenser plates, however, the field is never homogeneous. Let us suppose that the light passes through an arrangement corresponding to fig. 4, a vessel of

Fig. 4.



length m , and between the condenser plates of length l and thickness t . The distance between the plates is d . The potential difference between the plates is V . The action of the field on a common liquid can be expressed as follows:

$$\Delta = 2\pi B \int_{-\frac{m}{2}}^{\frac{m}{2}} E^2 dy. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This action is equivalent to a homogeneous field of intensity

$E_0 = \frac{V}{d}$ and of length l_0 :

$$\Delta = 2\pi B l_0 E_0^2. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus l_0 is defined and is evidently independent of the potential difference between the plates.

In the question of the disperse systems treated here, the quadratic law is often not applicable, but a more complicated one instead,

$$\Delta = 2\pi B l f(E).$$

Instead of (2) and (3) we obtain

$$\Delta = 2\pi B \int f(E) dy = 2\pi B f(E_0) \times l_0;$$

l_0 is a function of E , thus one cannot give any corrected value.

In the case of several colloids, however, the deviation from the quadratic law is slight, and therefore in order to get an idea of the order of magnitude of the correction $l_0 - l$, an estimate was made on the assumption that the expression (1) is valid.

In some preliminary experiments a tube very long in comparison with the condenser plates was used. If $m - l$ (cf. fig. 4) is a large quantity, the formula $l_0 - l = \frac{d}{\pi}$ of Lemoine * can be used.

On account of the very strong absorption which frequently occurs, it was necessary to work with as short layers of liquid as possible; so troughs were employed, the end surfaces of which were at a very short distance from the end surfaces of the condenser plates. For this case a correction formula has been given by L. Chaumont †:

$$l_0 - l = \frac{d}{\pi} \left\{ 1 + \frac{d}{\sqrt{a^2 - 1}} \log \left(a + \sqrt{a^2 - 1} \right) - \log \frac{az - 1 + \sqrt{z^2 - 1} \sqrt{a^2 - 1}}{z - a} \right\},$$

where z and a are defined by

$$m - l_0 = \frac{d}{\pi} \left\{ -\frac{\sqrt{z^2 - 1}}{a^2 - 1} + \frac{a}{\sqrt{a^2 - 1}} \log (z - \sqrt{z^2 - 1}) - \log \frac{az - 1 + \sqrt{z^2 - 1} \sqrt{a^2 - 1}}{z - a} \right\}$$

$$\frac{a}{\sqrt{a^2 - 1}} = 1 + \frac{2t}{d}.$$

* C. R. cxxii. p. 836 (1896).

† Thèses, Paris, 1914, p. 161.

For the meaning of the symbols, see fig. 4.

The values of one of the troughs used were as follows :—

$$m = 4.04 \text{ cm.}$$

$$l = 3.94 \text{ ,,}$$

$$d = 0.15 \text{ ,,}$$

$$t = 0.10 \text{ ,,}$$

$$l_0 - l = 0.33 \text{ ,,}$$

$$l_0 = 3.94 + 0.03 \text{ cm.}$$

As the correction for the length of the condenser does not reach one per cent., it obviously can be neglected when compared with the other sources of error and with the poorly-defined nature of the medium.

Electric Double Refraction in a Mercury Sol.

A mercury sol was prepared by the method of pulverization according to Bredig*. The experimental arrangement was that described by I. Nordlund†. As dispersion medium, water of conductivity $0.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ was used. The plane mercury surface served as a negative electrode. The intensity of the current was about 2.8 amperes. The temperature of the water was 1° and at the end of the pulverization 5° . Thus a fairly stable sol was obtained. On p. 66, fig. 11c, of Nordlund's paper the distribution curve for a sol prepared according to the same method is reproduced. The sol thus obtained was diluted with water of the same conductivity as that used in the pulverization; so that the final concentration was 2.0×10^{-5} gram per cubic centimetre.

The sol shows negative double refraction in an electric field. For the measurements a trough was used with the dimensions :

$$l = 4.93 \text{ cm.}$$

$$m = 5.04 \text{ ,,}$$

$$d = 0.236 \text{ ,,}$$

The wave-length used was $K = 5750 \text{ \AA.U.}$ (Filter from Wratten & Wainwright.) The data of the measurements are found in Table II., where P is the potential difference in volts, and Δ is the phase difference in minutes of arc.

* *Z. f. Electroch.* iv. p. 514 (1898).

† *Inaug.-Diss.*, Upsala, 1918.

TABLE II.

*Electric double refraction in mercury sol.*Wave-length = 5750 Å.U. ; Concentration = 2.0×10^{-5} gram per cubic centimetre.

P. (volts.)	-Δ.	$-\frac{\Delta}{P^2}$.	$-\frac{\Delta}{P}$.
23	70'	0.132	3.0
40	154'	0.096	3.6
50	226'	0.091	4.5
60	261'	0.073	4.3
68	280'	0.061	4.1
100	330'	0.033	3.3
145	396'	0.019	2.7

As will be shown later on, water exhibits a positive double refraction which is a function of the quantity of electrolyte in the solution. The mercury sol showed a conductivity not greater than 2.5×10^{-6} ohm⁻¹ cm.⁻¹. As will be shown later (*cf.* Table XII.), a sodium-chloride solution of this conductivity shows a positive double refraction of about 5' in a field of about 100 volts per 0.236 cm. Nothing is known of the nature of the electrolyte in the sol. It appears probable however, that the double refraction arising from the dispersion medium is slight compared with that in the sol.

Table II. shows that Δ increases with the intensity of the field, but not quadratically, as is the case in common liquids and in gold sols when the intensity is small. It appears more likely that the double refraction is proportional to the intensity of the field.

This very strong double refraction of the mercury sol is especially remarkable. It is generally assumed that these particles are spherical. Thus there should be no question of any effect of orientation. There is the possibility, however, that the particles do not consist of mercury, but of mercurous oxide. I. Nordlund * has thoroughly investigated the method of preparation. He found in a sol prepared at a temperature of 110° that the ratio between the quantity of mercurous oxide and the quantity of metal is 1:14,000. Hence there is no doubt that the effect should be ascribed to the mercury particles. If double particles occur, one might imagine an orientation on account of the field. It should, however, be remembered that the result of such an orientation should be a phase difference which is quadratically dependent on the

* Inaug. Diss., p. 78. Upsala, 1918.

intensity. This is not at all the case. A direct electro-optical effect might be possible. It remains, however, to take into consideration the electro-capillary phenomenon first described by Christiansen*. A mercury drop surrounded by an electrolyte solution of diluted sulphuric acid becomes deformed if a voltage is applied between two electrodes in the solution. The drop becomes egg-shaped, with the pointed end towards the positive pole. The deformation increases with the intensity of the current.

In this connexion the behaviour was observed of a drop of mercury under the influence of alternating voltage. In one experiment a mercury drop surrounded with water of conductivity $0.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ was observed. The electrodes were of platinum and were placed at a distance 1.0 cm. from each other. The diameter of the drop was 0.25 cm. The edge of the drop was examined under the microscope. When alternating current of 1200 cycles per second and a pressure of 150 volts was used, no elongation was noted. (The maximum elongation must be less than 0.0004 cm.) In a solution of sulphuric acid of the concentration 0.223 gram per litre, trembling of the drop was obvious when using a voltage drop of 40 volts per cm., but no elongation could be detected. In a sulphuric acid solution of higher concentration, on the other hand, an appreciable change of shape could be seen. In a solution of the concentration 2.22 grams sulphuric acid per litre, an elongation of 0.020 cm. was observed when the potential difference was 10 volts.

We may conclude from the experiments that it is the intensity of the current and not that of the field which is of importance for the elongation. This agrees with our experience of the change of the surface tension with the intensity of the field.

A possibility exists that it is a question of a directed disturbance of the double layer of the micell, which is covered by a gas-layer on the sides facing the electrodes. The writer certainly has not observed any such phenomenon on mercury drops of microscopic dimensions. Such a disturbance would cause the dielectric constant parallel to the field to be less than that at right angles to the field.

Gold Sols.

When an attempt is made to obtain, by the same means as used with common liquids, an exact value of the phase

* *Annal. d. Phys.* [4] xii. p. 1072 (1903).

difference by the aid of repeated measurements on the same portion of colloid, the values obtained gradually decrease. The colloid is changed during the influence of the field. A provisional explanation of this may be the change of temperature caused by the flow of current. The phase difference should decrease with increased temperature. If the liquid in the trough is allowed to cool, it will be found that the original value cannot be reproduced. The colloid must have undergone more fundamental change. Coagulation resulting from a difference in mobility of the micellæ is excluded. Investigations on cataphoresis show that the translational movements of the particles are independent of the size*. These gold sols are characterized by a certain instability when they are brought into contact with molar gold. Perhaps the diminution of concentration at the electrode plates, owing to the precipitation, is the cause of the phenomenon. This diminution is perhaps equalized in the whole volume of the liquid through diffusion and convection currents.

For the measurements on the gold sols a trough of the following dimensions was used:—

Length of trough m	(cf. fig. 4)	= 4.04 cm.
„ „ plates l	„ „	= 3.94 „
Distance between plates d	„ „	= 0.165 „
Thickness of plates t	„ „	= 0.10 „

Preparation of the Gold Colloids.

In order to prepare the gold sols, specially purified water was used. Ordinary distilled water was redistilled, first with the addition of potassium permanganate and sulphuric acid, then with the addition of barium hydroxide, and finally in an apparatus of Jena glass. The conductivity of the water obtained in this way was about 1×10^{-6} ohm $^{-1}$ cm. $^{-1}$. All the sols were prepared in flasks of Jena glass, which, after being carefully cleaned with boiling aqua regia and chromic acid, were finally boiled with distilled water. To obtain the sols, Zsigmondy's nuclear method was employed, using the following solutions:—

HAuCl $_4$ 0.01 mol. per litre.

K $_2$ CO $_3$ 0.1 mol. per litre.

H $_2$ O $_2$ 30 per cent. (perhydrol from Merck).

A saturated solution of phosphorus in ether, diluted to 1/5.

* Cf. The Svedberg and Hugo Anderson: *Koll. Zeitschr.* xxiv. p. 156.

The first colloid in a series was prepared using the phosphorus solution as a reducing agent, the following with the aid of the hydrogen peroxide solution. The latter reaction has been studied by F. Doerinckel* and A. Vestgren†. The sol No. 1 was prepared according to the following scheme:—

HAuCl ₄ solution	...	1	cubic centimetre.
K ₂ CO ₃	„	0.5	„ „
Water		98.5	„ „
P-solution		0.5	„ „

After the lapse of about twelve hours the solution was boiled in order to remove the ether, and a current of filtered air was passed through it in order to oxidize the phosphorus. Then a few cubic centimetres of water were added to obtain a sol containing 1.96×10^{-5} gram gold per cubic centimetre. The product was a sol of a characteristically light red colour. Starting from this nuclear liquid a series of colloids was produced with increasing size of particle. Thus sol No. 2 was prepared with the aid of No. 1 as a nuclear sol. Generally speaking, if

r_i	=	the radius of the particles in the nuclear sol	($m\mu$);
r_j	=	„ „ „ „ resulting sol	($m\mu$);
y	=	volume of nuclear sol	(cubic centimetres);
x	=	„ „ HAuCl ₄ „ „	
m	=	„ „ the mixture „ „	
C	=	„ concentration of HAuCl ₄	(gram gold per cubic centimetre);
c_j	=	„ „ the nuclear sol „ „	
c_i	=	„ „ „ resulting sol „ „	

we obtain x and y by the equations

$$y = m \frac{c_j}{c_i} \left(\frac{r_i}{r_j} \right)^3,$$

$$x = m \frac{c_j}{C} \left(1 - \frac{y}{m} \frac{c_i}{c_j} \right).$$

* *Zeitschr. f. anorg. Chemie*, lxiii. p. 344 (1908).

† *Zeitschr. f. anorg. Chemie*, xciii. p. 151 (1915).

Thus the scheme for the preparation of the sol No. *j* appears as follows :—

y cubic centimetres nuclear solution ;
x „ „ HAuCl_4 ;
(*m* − *y* − *x*) „ „ water ;
2 drops hydrogen peroxide per 100 cubic centimetres solution.

The sols investigated contained 1.96×10^{-4} gram gold per cubic centimetre.

TABLE III.

Electric double refraction in gold sol.

Wave-length = 5900 Å.U. ; Concentration = 1.96×10^{-5} gram gold per cubic centimetre ; Diameter $2r = 106 \text{ m}\mu$.

P. (volts.)	−Δ.	− $\frac{\Delta}{P^2}$.
7.9	9'.4	0.15
11.6	27'.9	0.21
17.1	55'.6	0.19
21.6	86'.1	0.18
30.0	133'	0.15
35.0	171'	0.14
45.0	205'	0.10
51.2	216'	0.083
66.0	233'	0.053
84.0	242'	0.032

In Table III. and fig. 5 some data are shown relating to the effect of the potential difference on the electric double refraction in a coarse-grained sol, $2r = 106 \text{ m}\mu$ *. In fig. 5 the potential differences *P*, measured in volts, are plotted as abscissæ, and the phase differences Δ as ordinates. Δ is given in minutes of arc. The double refraction is negative. For small values of the potential difference the phase difference is approximately proportional to the square of the intensity, but afterwards approaches a saturation value. The

* $\text{m}\mu = \text{millimicron} = 10^{-7} \text{ cm.}$

Fig. 5.

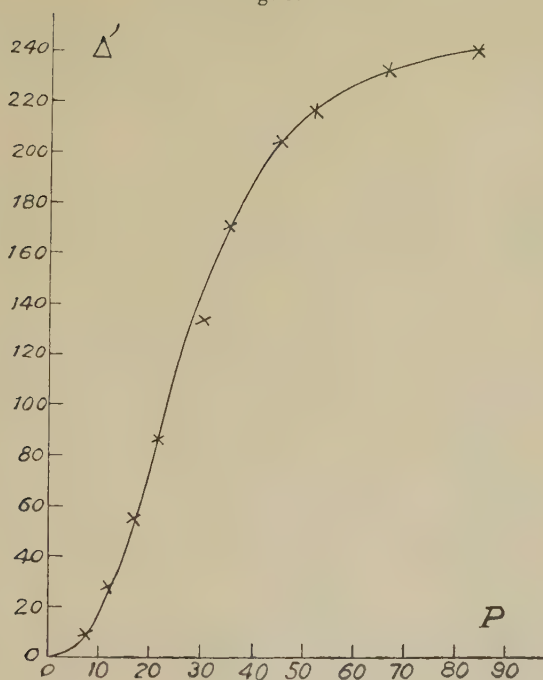


TABLE IV.

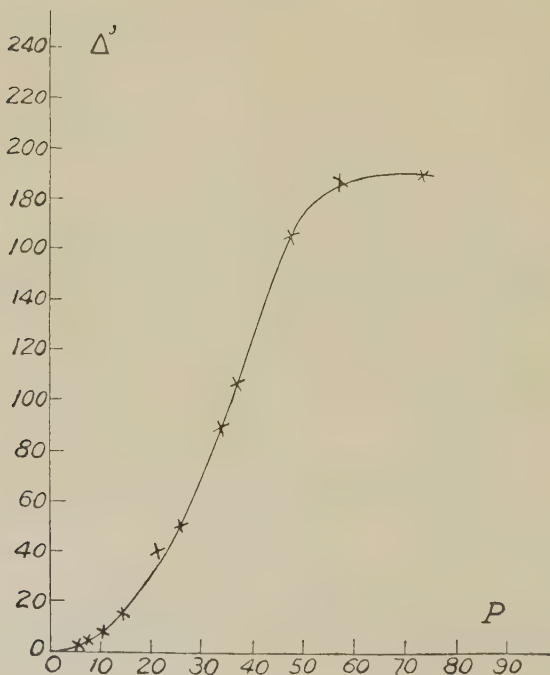
Electric double refraction in gold sol.

Wave-length = 5900 Å.U. ; Concentration = 1.96×10^{-5} gram gold per cubic centimetre ; Diameter $2r = 53 \text{ m}\mu$.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.
5.2	3.4	[0.13]
7.8	4.1	0.067
10.1	9.7	0.086
14.8	14.7	0.067
21.6	37.8	0.081
26.0	50	0.075
34.0	89	0.077
38.0	105	0.073
48.0	164	0.072
57.5	186	0.056
74.3	188	0.054

measurements were carried out with the use of the wave-length 5900 Å.U. Table IV. and fig. 6 represent the values which were obtained from observations on a sol of high dispersity, $2r=53\text{ m}\mu$. Even here saturation sets in.

Fig. 6.



The influence of the size of the particles is very pronounced. Whereas sols with the particle coefficient $2r=5\text{ m}\mu$ and $2r=15\text{ m}\mu$ showed hardly any measurable effect at a potential difference of 20 volts, for a sol characterized by $2r=53\text{ m}\mu$ a value of $\Delta=38'$ was found, and for a sol $2r=106\text{ m}\mu$ a value of $\Delta=86'$. For sols containing particles of the size $200\text{ m}\mu$ the double refraction under the same conditions attains a value of $\Delta=5^\circ$. A series of measurements illustrating the variation of the effect with change in size of particle are recorded in Table V.

The change of the double refraction with wave-length is also striking. Only one diagram illustrating the dispersion

is reproduced here (Table VI. and fig. 7). The effect shows a very distinct maximum at about 6000 Å.U. The wave-length was varied by means of the monochromatic illuminator.

TABLE V.

Variation of electric double refraction with size of particles.

Wave-length $\lambda = 5900$ Å.U. ; Concentration $= 2.0 \times 10^{-5}$ gram gold per cubic centimetre ; Temperature $17^{\circ}5$ C.

$2r$. ($m\mu$.)	P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.
130	13.6	39'.0	0.39
,,	20.2	123'.0	0.30
65	13.4	29'.0	0.16
,	19.2	59'.2	0.16
32	12.6	5'	0.031
,	18.6	6'	0.017
20	18.4	1'	0.003

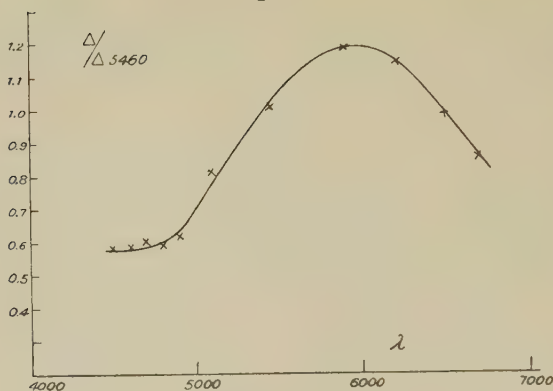
TABLE VI.

Dispersion of double refraction in gold sol.

Potential difference $P = 23.9$ volts ; Diameter $2r = 106 m\mu$;
Concentration $= 0.98 \times 10^{-5}$ gram per cubic centimetre.

Wave-length. (Å.U.)	$-\Delta$.	$\Delta/\Delta 5460$.
6700	30'	0.85
6500	34'	0.98
6220	40'	1.14
5900	41'	1.18
5460	35'	1.00
5100	28'	0.81
4900	22'	0.61
4800	21'	0.59
4700	21	0.60
4600	20'	0.58
4500	21'	0.59

Fig. 7.

*Sulphur Sols.*

In the following an account is given of some measurements on a colloid, or more properly, a suspension, with a non-metallic disperse phase, viz. sulphur. The sols were prepared according to Pihlblad's* homœopathic method. The same trough that had been used for the gold sols was employed for the measurements. Some data are given in Table VII. The double refraction is negative. The suspension contained 8.0×10^{-5} gram sulphur per cubic centimetre. The particle coefficient was $2r=360 \text{ m}\mu$. The wave-length of the light used was $5900 \text{ \AA.U.}$ Here the deviation from the quadratic law can be traced. Δ/P^2 decreases with the potential difference.

TABLE VII.

Electric double refraction in sulphur sols.

Wave-length = $5900 \text{ \AA.U.}$; Concentration = 8.0×10^{-5} gram sulphur per cubic centimetre; Diameter $2r=360 \text{ m}\mu$.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$
4.0	0'	0
7.6	16'	0.28
11.6	37'	0.27
13.6	39'	0.21
15.4	46'	0.19
17.1	58'	0.20
19.2	67'	0.18
22.9	71'	0.10
26.6	69'	0.10
16.0	49'	0.19

* Cf. N. Pihlblad, Dissertation, Upsala, 1918.

In Table VIII. some values of the electric dichroism are given. The component parallel to the field is mostly absorbed. Tables IX. and X. represent data from experiments with a more fine-grained sol containing 4.1×10^{-6} gram sulphur per cubic centimetre and of the particle coefficient $2r=190 \text{ m}\mu$. The effect here is considerably less than in the previous solution. It should be observed that a maximum phase difference exists for a certain potential difference. The phenomenon can be attributed to the double refraction of water.

TABLE VIII.

Electric dichroism of sulphur sol.

Wave-length = $5900 \text{ \AA.U.}$; Concentration = 8.0×10^{-5} gram sulphur per cubic centimetre; Diameter $2r=360 \text{ m}\mu$.

P. (volts.)	ϕ .
20.0	0
34.0	12'
53.0	48'

TABLE IX.

Electric double refraction in sulphur sol.

Wave-length = $5900 \text{ \AA.U.}$; Concentration = 4.1×10^{-6} gram sulphur per cubic centimetre; Diameter $2r=190 \text{ m}\mu$.

P. (volts.)	$-\Delta$.	P. (volts.)	$-\Delta$.
3.6	0'	17.5	4'
5.6	0'	27.0	9'
9.1	0'	37.0	12'
13.0	0'	45.0	13'
18.4	5'	56.0	11'
21.6	8'	102.0	9
27.4	8		

TABLE X.

Electric dichroism of sulphur sol.

P. (volt.)	ϕ .
35.0	4'
76.0	18'

P-Azoxyphenetol Sol.

The systems obtained by pouring an alcoholic solution of *p*-azoxyphenetol into water are characterized by the size of the particles, which can be varied by changing the concentration of the alcoholic solution, and further by the length of time the sol is preserved. The nature of these sols is not fully established. Does the disperse phase consist of crystals or is it still liquid? Certain coagulation experiments seem to hint at the possibility of the latter alternative; the particles in the sol would thus consist of liquid—it would be an emulsion. Now *p*-azoxyphenetol belongs to those substances which between certain limits of temperature become crystalline liquids. It would then be a matter of a disperse system with particles consisting of under-cooled crystalline liquid.

In an electric field such sols show a very strong double refraction of negative sign, which is considerably greater than that obtained even with a rather coarse-grained sol obtained by the method of Pihlblad*.

Double Refraction of the Dispersion Medium.

An account has been given in the preceding pages of the electric double refraction in gold, mercury, and sulphur sols. Only these three typical cases are considered here, for the following reasons:—

When discussing the double refraction of a colloid it is necessary first of all to discuss the effect which arises on account of the disperse phase and the dispersion medium separately. The Kerr constant for common liquids is, however, of such an order of magnitude that the Kerr effect in the weak fields here used can be neglected. Direct experiments with conductivity water and with very dilute solutions showed, however, a number of anomalies. The double refraction is strong and a function of the concentration of the electrolyte. Probably we can obtain an idea of the latter in a colloidal solution from the electrical conductivity. Unfortunately the investigations on water were not made until after those on the double refraction of the sols were already completed.

It was found, when investigating the double refraction in certain gold sols, that the sign of the phase difference was negative at first but afterwards became positive. Such a sol contains particles of the size $2r=106\text{ m}\mu$. Fig. 8 illustrates the phenomenon when the voltage between the condenser plates was 36.0 volts. The double refraction first

* *L. c.* p. 46.

increases, then reaches a maximum on the negative side, decreases to zero, and lastly assumes a definite positive value. The reverse is the case when the voltage is switched off and the plates are grounded, this being illustrated by fig. 9. The phase difference first increases, reaches a maximum, and thereafter falls to zero. The process strikes one as being very curious. The form of the curve indicates that there are two concurrent phenomena. A systematic fractional sedimentation showed that there could be no question of two kinds of particles. Hence the phenomenon must be ascribed

Fig. 8.

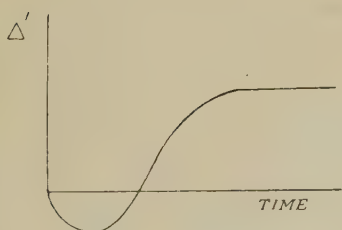
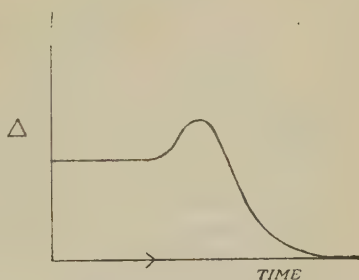


Fig. 9.



to the antagonism between the double refraction of the disperse phase and that of the dispersion medium. Now it is known that water shows positive double refraction*, but the results obtained are very dubious on account of the considerable conductivity. According to W. Schmidt† we have for the Kerr constant of water

$$B = B_0 \times 1.0,$$

where B_0 is the constant for carbon disulphide, for which we may assume a value

$$B_0 = 3.2 \times 10^{-7} \dagger.$$

In a field of intensity $E=100$ volts per 0.25 centimetre we may expect a phase difference of

$$\Delta = 2\pi B l \left(\frac{E}{300} \right)^2,$$

amounting only to about 0.06 [$l=5.0$ cm.]. It may be said that the most characteristic feature of the Kerr effect is its

* Cf. J. Kerr, *Phil. Mag.* (5) xiii. pp. 153 & 248 (1882).

† *Annal. d. Phys.* vii. p. 142 (1902).

Cf. L. Chaumont, *Thèses*, Paris, 1914.]

very short time of appearance. Abraham and Lemoine* have shown that for carbon disulphide the time of appearance is less than 10^{-8} second. Later on, James† has shown that the disappearance of the double refraction may be supposed to be instantaneous. Thus the conclusion could not be drawn that the form of the curve depended upon the concurrence between a negative double refraction, due to the colloidal particles, and a positive double refraction due to the common Kerr effect in the dispersion medium. Therefore an investigation was begun on the behaviour of water in an electric field, and some very peculiar phenomena were discovered. Common distilled water from the supply of the laboratory, with an electrical conductivity of 4.3×10^{-5} ohm $^{-1}$ cm. $^{-1}$, showed greater double refraction than water prepared with special care, the conductivity of which was reduced to 0.85×10^{-6} ohm $^{-1}$ cm. $^{-1}$. In other words, the phase difference is a function of the conductivity of the electrolytic concentration.

Using water of conductivity 0.80×10^{-6} ohm $^{-1}$ cm. $^{-1}$, a series of sodium-chloride solutions of a concentration varying between 0 and 5×10^{-4} N. was prepared, and the electric double refraction of these was studied. A trough was used with the following dimensions :—

Distance between plates $d = 0.236$ centimetre.

Length of plates $l = 4.94$ „

Depth of liquid layer $L = 5.04$ „

The wave-length of the light used was 5900 Å.U. The data are reproduced in Tables XI.–XVII. It is evident from Table X. that the double refraction of the pure distilled water does not reach a definite value at once. The increase with time is here, however, comparatively insignificant. At a higher concentration this increase becomes more evident. In a 2.0×10^{-4} normal sodium-chloride solution, for example, the phase difference is 7'.8 after a lapse of 5.0 seconds, and 27'.2 after 45 seconds. Now, it must be remembered that the solution is heated by the current. Considering the influence of the temperature we have, according to Langevin's‡ theory, which at least approximately accounts for the conditions involved, $B = \frac{A}{T}$, where B is the Kerr constant and A is a constant independent of temperature T.

* Cf. *C. R.* cxxix. p. 206 (1899).

† *Ann. d. Phys.* iv. p. 954 (1904).

‡ *Le Radium*, vii. p. 251 (1910).

TABLE XI.

Electric double refraction of water.

Wave-length = 5900 Å.U.; Conductivity = 0.85×10^{-6}
ohm⁻¹ cm.⁻¹; Potential difference = 100 volts.

Time. (sec.)	Δ.
15	1'6
30	3'1
45	2'9
75	3'4
90	3'7
120	3'7

TABLE XII.

Electric double refraction of 0.1×10^{-4} normal sodium-chloride solution.

Conductivity = 2.34×10^{-6} ohm⁻¹ cm.⁻¹;
Potential difference = 100 volts.

Time. (sec.)	Δ.
10	5'7
30	8'1
45	8'1
60	7'8
90	7'8
120	7'8

TABLE XIII.

Electric double refraction of 0.5×10^{-4} normal sodium-chloride solution.

Conductivity = 6.7×10^{-6} ohm⁻¹ cm.⁻¹;
Potential difference = 100 volts.

Time. (sec.)	Δ.
5	4'7
20	15'2
30	15'2
45	13'8
60	13'8
120	13'8

TABLE XIV.

Electric double refraction of 10×10^{-4} normal sodium-chloride solution.

Conductivity = 12.3×10^{-6} ohm $^{-1}$ cm. $^{-1}$;

Potential difference = 100 volts.

Time. (sec.)	Δ .
5	7'3
15	17'6
30	20'4
45	23'0
60	20'4
90	17'8
120	20'1

TABLE XV.

Electric double refraction of 2.0×10^{-4} normal sodium-chloride solution.

Conductivity = 22.1×10^{-6} ohm $^{-1}$ cm. $^{-1}$;

Potential difference = 100 volts.

Time. (sec.)	Δ .
5	7'8
30	30'8
45	27'2
75	27'2
90	23'5
120	27'2

TABLE XVI.

Electric double refraction of 5×10^{-4} normal sodium-chloride solution.

Conductivity = 50.6×10^{-6} ohm $^{-1}$ cm. $^{-1}$;

Potential difference = 100 volts.

Time. (sec.)	Δ .
5	17'5
30	28'0
90	22'2
120	28'2

TABLE XVII.

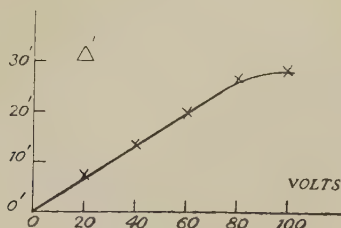
Electric double refraction of 5×10^{-4} normal sodium-chloride solution.

$$\text{Conductivity} = 50.6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}.$$

Potential difference, (volts.)	Δ .
20.0	7'6
40.0	13'3
60.0	19'8
80.0	26'6
100.0	28'0

In the case of the common Kerr effect, a decrease of the double refraction should occur with increased temperature. Thus it must be another phenomenon, and the dependence of the effect on the intensity of the field also shows this. Table XVII. shows (*cf.* also fig. 10) that the phase difference is nearly proportional to the potential difference, while with the common Kerr effect the quadratic law holds true. In Table XVII. the phase difference is recorded as measured 30 seconds after the voltage has been applied.

Fig. 10.



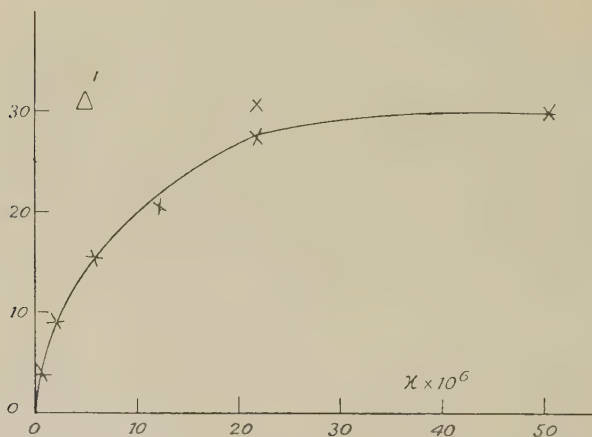
The influence of the conductivity is very surprising. Fig. 11 shows the double refraction, measured 30 seconds after the voltage has been applied. The phase differences are plotted as ordinates and the conductivities as abscissæ. The double refraction rises with the concentration and the conductivity, from the slight value corresponding to the distilled water to a value of saturation answering to the more concentrated solutions.

The determinations made are more of an orientating character, and it is perhaps premature to advance any theory in respect to the phenomenon. It is not probable that the Na or Cl ions could directly give rise to double

refraction. The concentration of the ions is very insignificant. The effect probably is connected instead with the hydration of the ions, and the migration of these large aggregates through the liquid. The water molecules along the path of the aggregates are oriented. The author has previously advanced the same hypothesis in regard to certain crystalline liquids*.

On the whole it is a delicate matter to make measurements on liquids of a conductivity of this magnitude. As a matter of fact, colloids in general contain a certain, even if a small, quantity of electrolyte. It is therefore necessary to find out

Fig. 11.



the behaviour of the dispersion medium with addition of electrolytes before attempting to estimate the combined effect.

Through consideration of the very peculiar double refraction in water it is easy to explain the strange curves of relaxation in the case of gold sols (*cf.* figs. 8 and 9). The negative double refraction which appears when the voltage is applied can be attributed to the gold particles. Gradually the positive effect from water sets in, and the resulting phase difference becomes zero and eventually positive, all of which depends upon the gold concentration, the degree of dispersity, and the concentration of electrolyte. A reverse process takes place when the voltage is cut off.

There are many different problems which remain to be examined, but mention will be made of only one, viz. the coagulation. Owing to the conductivity being considerable

* Cf. *Ann. der Phys.* (4) lvi. p. 202 (1918).

the disturbances are also large. It is necessary to examine the double refraction of the electrolytes before the curves of the colloids can be discussed. Therefore no values will be given here. Perhaps a higher frequency than 1200 cycles per second is necessary to prevent the decomposition.

Further mention may be made of some investigations of systems with the same disperse phase but different dispersion media. Here should be obtained a relation with the dielectric constant. Other questions are the variation of the effect with the wave-length, *i. e.* the dispersion and the influence of temperature and time.

In the preceding tables were given the potential difference P and also the distance between the plates d , but not the intensity of the field E . For these conducting liquids one is not justified, without further investigation, in putting

$E = \frac{P}{d}$ for a point in the liquid. A considerable potential

drop may occur at the electrodes. Some experiments have been made in order to analyse this problem by varying the distance d between the plates, but no definite results have been obtained on account of the instability of the systems used.

It seems obvious that the electric double refraction may be attributed to an orientation of particles of asymmetrical shape or structure. Let us only consider the first case: isotropic particles of asymmetrical shape. The influence of the forces acting on the particle should then be analysed. In the field the largest axis of the ellipsoid has a tendency to place itself parallel to the lines of force. This is one possibility. Now the particle is charged. Cataphoresis takes place owing to the influence of the field. We know that a body of asymmetrical shape moving in a liquid tends to place its greatest axis at right angles to the direction of the movement. Thus two concurring forces act upon the particle. By comparison with certain experiments on mechanical double refraction* it can be decided that a negative double refraction in gold sols points towards an orientation of the greater axis parallel to the lines of force. "Points towards" is written intentionally; many sols, for example mercury or platinum, which show no trace of flowing effect, still exhibit a pronounced negative electric double refraction. An asymmetrical shape of these particles cannot at present be determined by experiment and is rather improbable in

* Cf. Phil. Mag. xlii. p. 362 (1921).

mercury sols. It is necessary to conclude that, at least in certain cases, an electro-optical effect in the classical sense is not impossible. The experiments carried out on double refraction of gold sols with the addition of gelatine show the existence of a time of relaxation. Gelatine sols and gels, however, also show electric double refraction, but of the opposite sign, and they exhibit, besides, very disturbing phenomena: a strong formation of striæ. In any case the experiments show that orientation plays an important role, at least in the case of gold sols.

A further support for this is the fact that the dispersion curve shows an evident similarity to that of the magnetic double refraction. The author has shown that the latter phenomenon is caused by an orientation*. From the above point of view it is not difficult to advance a theory on the electric double refraction corresponding to the writer's theory for the effect in a magnetic field†. On account of the complexity of the electric double refraction, however, the theory is not given here.

It is obvious that the phase difference in the question of gold sols (*cf.* fig. 6) approaches saturation with increasing intensity of the electric field. Considering the different factors, we may imagine, for example, that the parallel orientation of the particles begins to reach completion under the influence of the field. Another alternative is that the cataphoretic action plays a part, which tends to orientate the particle at right angles to the field. Finally, the effect in the dispersion medium is very important. The latter is positive for water, and it is here that we must search for the fundamental reasons for the deviation from the quadratic law.

As a final remark, it may be stated that the electric double refraction in colloids is of great interest, but in itself has not yet enabled us to arrive at any conclusions regarding the structure of the colloidal particle. The phenomenon is too complicated; too many factors are playing a part. To analyse the nature of the electric double refraction, we should instead be guided by the phenomena in the magnetic field, where the disturbances are not so great.

* *Cf. l. c.*

† *Cf.* "On Accidental Double Refraction in Colloids," Upsala, 1924.

LXI. *An Oscillographic Study of Anodic Polarization.* By
V. H. L. SEARLE, M.Sc., Asst. Lecturer in Physics, Univ.
College of the South-West of England*.

1. INTRODUCTION.

THE phenomenon of anodic polarization and its application to the rectification of alternating current have attracted the attention of many investigators, and the main features of the effect may now be considered to be well established although there are still differences of opinion as to its exact cause. In 1914 G. Schulze and R. Lindemann† put forward a view involving electronic processes in an exceedingly thin gas film on the surface of the valve metal. A short time later C. W. Greene‡ carried out measurements on the counter e.m.f. at extremely small intervals of time after charging, and concluded that this back e.m.f. is alone sufficient to account for the current reduction. The results obtained seemed to be in accord with the gas film and ionic diffusion theories. It was also shown in the same year by G. Schulze§ that total rectification does not occur, i. e. that the valve action is incomplete. A. L. Fitch|| in 1917 made potentiometer measurements of the counter e.m.f. with aluminium in saturated sodium phosphate solution. His results indicated that any method of experiment in which an appreciable time must elapse during the taking of data will introduce serious errors owing to changes occurring in the cell. In the same paper a theory was advanced of a double dielectric one part of which changes with the time of open circuit and the other with the time of closed circuit. F. Streintz¶ traced a close similarity between this case and the unipolarity observed with crystals of sulphides and metals, and he concluded that the polarization appears to be partly galvanic and partly dielectric—the latter being due, according to G. Schulze, to a film of oxide and to gaseous oxygen in the film. Schulze** regarded the formed anode as a condenser of high capacity and resistance. The resistance of the oxide film layer is small compared with that of the gas layer, and the ohmic resistances are by no means

* Communicated by Prof. F. H. Newman, D.Sc.

† *Phys. Zeitschr.* xv. p. 254 (1914).

‡ *Phys. Rev.* iii. ser. 2, p. 264 (1914).

§ *Archiv f. Electrot.* iii. p. 43 (1914).

|| *Phys. Rev.* ix. p. 15 (1917).

¶ *Phys. Zeits.* xxi. p. 471 (1920).

** *Phys. Zeits.* xxii. p. 146 (1921).

constant. To investigate the completeness of rectification produced by the valve action of a formed anode, F. H. Newman* carried out an oscillographic study, using aluminium and nickel electrodes in dilute sulphuric acid, and it appeared from his results that rectification is complete within the limits of current measurement possible with an oscillograph record. Recently, J. A. Crowther and R. J. Stephenson† concluded that the high resistance of a polarized electrode is due entirely to a gas film.

2. EXPERIMENTAL.

The two main features of the polarization effect with which the present experiments are concerned are the rate of formation of the electrode by means of direct current and the degree of recovery of the cell following a cessation of the current. Incidentally both experiments test the completeness of polarization produced by the employed current densities, and give an indication of the effectiveness of an electrolytic rectifier at low alternation frequency.

For all the experiments the electrolyte used was a saturated solution of ammonium phosphate with a nickel cathode in combination with an anode of aluminium. The same cathode was used throughout, but the surface area of the anode was changed to effect an alteration in the current density. Although, in practice, the whole series of readings for a given size of anode was carried out before a change was made in the anode, it would be convenient here to describe the comparative results obtained for the same kind of experiment rather than for the same electrode.

In investigating the rate of formation of the anode, a simple time and current reading was taken. At a noted instant contact was made in a circuit containing a battery of about 20 volts, the electrolytic cell with an anode of new polished aluminium, and a large range milliammeter. The current value was noted every 5 seconds for the first minute, and then at greater intervals until a steady state was reached. The current was then left on for about 12 hours, to note any slow creep. The same experiment was later performed with another fresh anode of different surface area.

To investigate the power of recovery which the cell possesses when the current is switched off, some arrangement was required by means of which contact could be

* Phil. Mag. xlix. p. 1029 (1925).

§ Phil. Mag. xlix. p. 1066 (1925).

made after a definite recovery period, and at the same time current records could be made at exceedingly small time-intervals after the current recommenced to flow. The oscillograph offered a convenient means of doing this, and accordingly a device was made to ensure that, when the falling plate reached the slit in the fall tube, contact in the electrical circuit was just made and the initial current form was recorded as an oscillogram. From a measurement of the curves made by a tuning-fork circuit in a previous investigation*, it was found that the plates fell in the camera with practically the same acceleration, which was only slightly less than that of free fall. This suggested the employment of a falling weight, released simultaneously with the plate, which should actuate a spring contact placed at the camera-slit level. The actual form of contact used comprised two steel springs carrying brass contact studs. These were normally kept from touching by a thin ebonite strip, which was mounted on one end of a rocking lever whose other end was depressed by the falling weight. This forced the ebonite from between the contact studs, and thus established the current. As a system of time coordinates the second vibrator of the oscillograph gave a trace of the tuning-fork current on the falling plate, as described in the previous paper†. The time of fall of the weight was known accurately and thus, since the time between the stoppage of the current and the release of the weight could be adjusted exactly, the whole interval during which no current flowed was known. To break the current at a noted time more exactly than could be done by the insertion of the ebonite strip between the contact studs, a key was placed in parallel with the latter and, with the strip in position for the falling weight, the recovery period began with the opening of the key.

621.

3. RESULTS.

(a) *Formation of Oxide Film.*

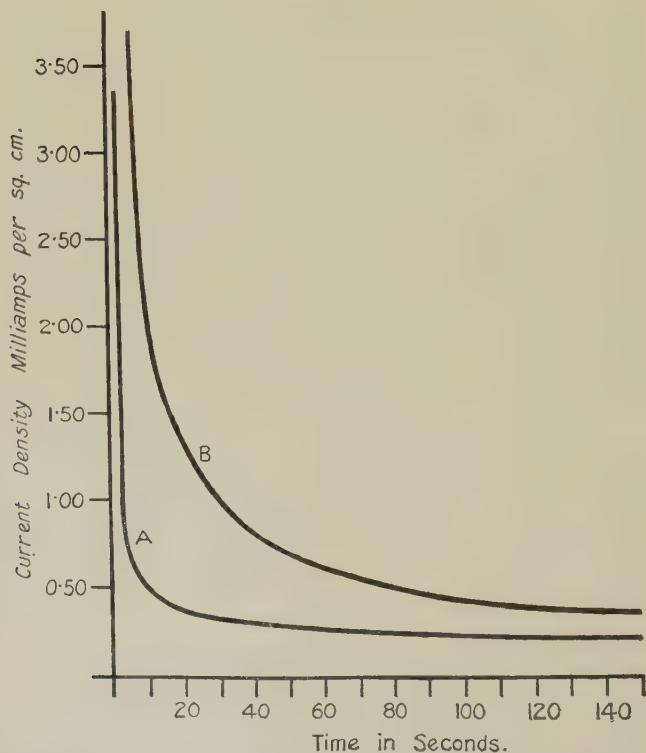
The connexion between current and time during the formation of the oxide film in the anode is shown in fig. 1. The curve A was obtained using an anode of surface area 140 sq. cms. with a battery of 18.6 volts, no resistance other than those of the electrolytic cell, the spring contact and the milliammeter being in the circuit. The rate of polari-

* V. H. L. Searle, *Phil. Mag.* 1. p. 738 (1926).

† *Loc. cit.*

zation is seen to be at first very rapid, since the current density was reduced to only twice its final small value—0.207 milliamps per sq. cm.—in about 11 seconds, while the final value was not attained until 180 seconds after making contact. This value was found to persist without change during the twelve hours' examination for any slow creeping effect. For the second experiment, the voltage was increased to 24.6 volts and the new anode surface area was 63 sq. cms. The resulting curve is shown at B, fig. 1,

Fig. 1.

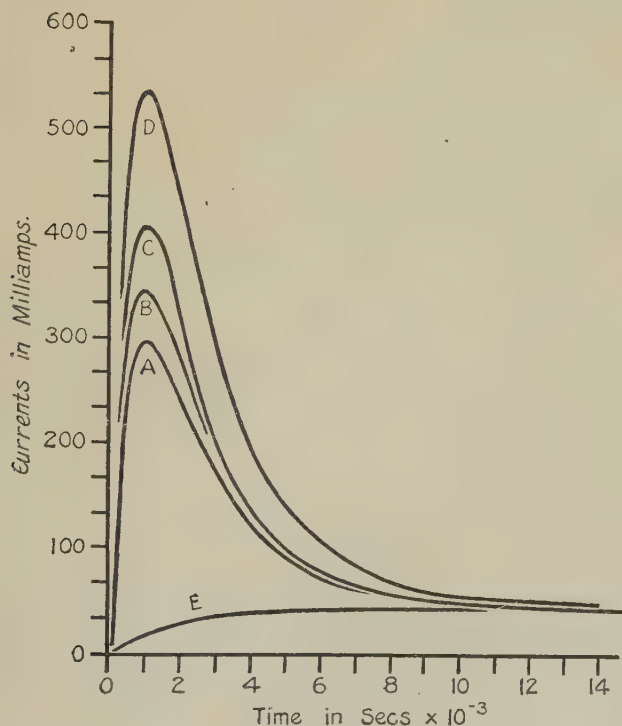


and it will be seen that the polarization effect in this case is less rapid, the time for the current to fall to twice its final value—0.159 milliamp. per sq. cm.—being now 145 seconds. In both cases no further change could be noticed in the current during twelve hours after the complete formation periods—3 mins. and 9 mins. respectively.

(b) *Depolarization Effect.*

Fig. 2 shows the result of the recovery which follows a cessation of the current after full oxide formation has recurred, and refers to the same anode as that of A, fig. 1. Curve A, fig. 2, was obtained from the oscillograph trace after the current had ceased for 1.5 secs. The other curves, B, C, and D of fig. 2, are the results of cutting off the current for 5.5, 15.0, and 30.0 secs. respectively. Curve E, fig. 2, indicates what would have been the result in all these

Fig. 2.

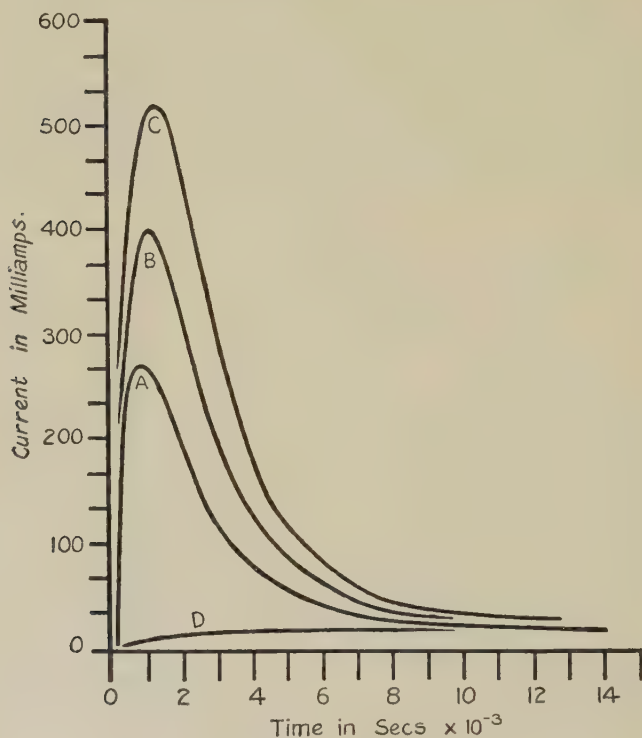


cases if no depolarization followed current cessation. The method of arriving at this curve is indicated later.

In fig. 3 similar graphs connecting current and time are shown for the anode of B, fig. 1. A, B, and C of fig. 3 refer to recovery periods of 30 sec., 3 mins., and 5 mins.

respectively, while D again shows, for comparative purposes, the curve for no depolarization.

Fig. 3.



4. DISCUSSION OF RESULTS.

(a) *Formation of Anode.*

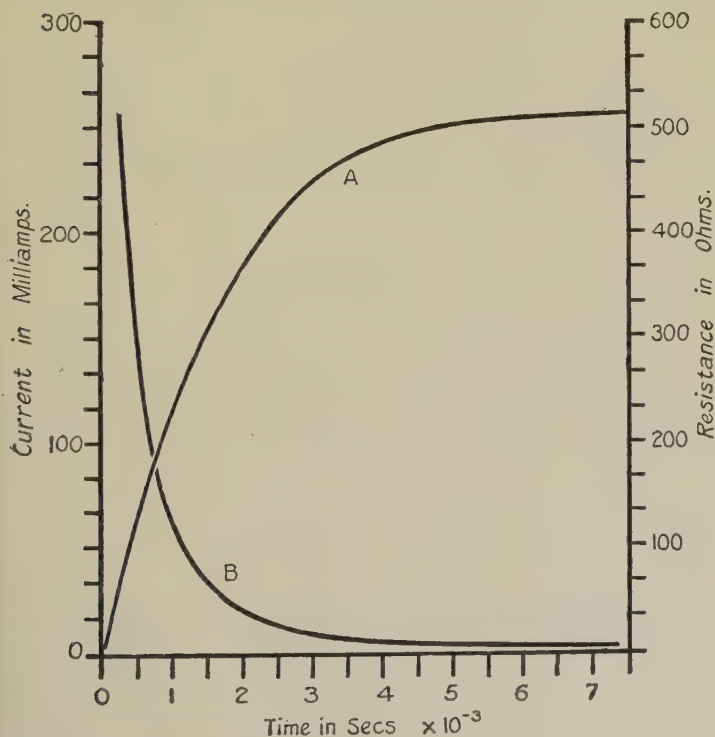
The first fact which becomes evident from a study of fig. 1 is the great rate of polarization, especially in the early stages of film formation, which occurs even in a previously polished aluminium surface. The result is the same as would have been obtained in the second series of experiments if the recovery had been complete, and the oscillograph curve would thus have had a very sharp peak. It would probably not be of very great value to modify the experiment to make an oscillograph record using a previously unformed anode, as the inertia of the moving system would prevent the mirror from following such a rapidly changing current. Comparison of the two curves shows a greatly lengthened time for steady conditions to be reached with increased voltage and decreased anode surface. Additionally, the fact that a steady state is reached before the current falls

to zero is in accordance with the statement of G. Schulze * that the valve action is incomplete although, for small surface areas, the rectification may appear, as in the experiments of F. H. Newman †, to be perfect.

(b) *Depolarization Effect.*

As would be expected, the degree of recovery depends on the time for which the current has ceased. This is indicated by the progressive changes shown by the curves of either fig. 2 or fig. 3. It should be remembered, however, in

Fig. 4.



studying these curves, that they are complicated by the time required for complete contact of the brass studs previously referred to. In order to investigate this factor, a separate record was obtained when the electrolytic cell was removed and contact was established in a circuit containing only a battery, the oscillator strip, and a non-inductive resistance. The result is shown in fig. 4, in which curve A gives the relation between time and current, while B associates time with the corresponding contact

* *Loc. cit.*

† *Loc. cit.*

resistance. From A, fig. 4, the comparison curves E, fig. 2, and D, fig. 3, were obtained. By combining the results shown in fig. 4 with those of either fig. 2 or fig. 3, the variation of the ohmic resistance of the electrolytic cell with time may be obtained, but no great accuracy is possible since at the specially interesting time—the stage when contact is first re-established—the contact resistance is changing too rapidly for exact calculation.

The smooth curves of figs. 2 and 3 were not obtained in every case, but sometimes irregular serrations appeared, particularly during the early part of the polarization period. These were attributed to bubbles of oxygen leaving the anode surface and thus altering the electrolytic resistance to a comparatively large degree. Later, when polarization is practically complete, a single bubble of oxygen would not greatly affect the now large resistance. This result seems to support the view of J. A. Crowther and R. J. Stephenson* that the polarization is due entirely to the large resistance of the gas film.

5. SUMMARY.

1. The rate of formation of anodic films has been studied, and it has been found that the valve action is not complete.
2. The final steady current density measured in milliamps. per sq. cm. per volt increases as the anode surface area increases.
3. Rapid recovery accompanies a cutting off of the polarization current. This indicates that the rectification of slow alternations would be incomplete.
4. The resistance of such an anode seems to be due almost entirely to the gas film formed on it.

The author wishes to express his thanks to Prof. F. H. Newman for suggesting this investigation and for the interest taken in its course.

* *Loc. cit.*

LXII. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MAY I call your attention to a paper of mine in the *Annal. d. Physik*, vol. lxxvii. p. 287 (1925), entitled "Ueber die Glimmentladung bei schnell wechselndem Feld," which covers the same subject as a recent interesting article (*Phil. Mag.* vol. ii. p. 129 (1926) : "A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures") by Messrs. E. W. Gill and R. H. Donaldson. These authors have measured the minimum potentials required to maintain a discharge in a gas at different pressures if oscillations of the order of $4 \cdot 10^7$ per second are used. They find that the minimum potential decreases continuously as the pressure is reduced (to about 50 volts at a pressure $p < \frac{1}{100}$ mm. of mercury). The authors are evidently not aware of my paper, which contains a large number of careful measurements of these potentials, obtained by a method which is capable of giving far more accurate results than the one which they employed. (My method involves the measurement of the deflexion of an independent cathode stream in a high vacuum.) The curves which I obtained show without doubt that the continuous decrease of the minimum potential with pressure obtained by the authors is solely caused by mercury vapour from the Toepler pump, which they evidently did not prevent from reaching the discharge-tube; and that the minimum potential rises again at a pressure of a few thousandths of a mm., if the mercury vapour is kept away. Moreover, I employed the "Continuous-flow" method of W. Wien, which eliminates perfectly the impurities that are always set free in a gaseous discharge.

May I also mention that the lowest potential with which I could maintain a discharge between cold electrodes, in neon gas for example, was 15 volts (lower than the ionizing potential).

Yours faithfully,

München,
August 12, 1926.

Dr. FRITZ KIRCHNER.

LXIII. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

PROFESSOR KIRCHNER has very kindly sent us a copy of his letter to you and we should like to express our regret that we had not previously seen his paper. We agree with him that the discharges we obtained with very low voltages were due to mercury vapour, in fact, we stated this specifically in our paper, and it is also evident that the potential must reach a minimum as the pressure is reduced, as no discharge could pass through an absolute vacuum.

We do not agree, however, that the deflexion of a cathode stream gives far more accurate measurements of alternating potentials than our method. Our method is capable of the greatest accuracy if the alternations are not too rapid, and it only becomes less accurate when the time of an oscillation is comparable to the time the electrons take to cross the measuring instrument; a limitation which applies equally to the cathode stream instrument. In addition, the latter only measures the electric force, while we measured the actual potential between the electrodes. When the discharge is passing the electric force is not uniform.

Yours faithfully,

Merton College,
Oxford.

E. W. B. GILL,
R. H. DONALDSON.

LXIV *The Water-Spark Absorption Spectrum of Iron.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I REGRET that I overlooked the paper on “*Spèctres d’étincelle dans l’eau*” by M. Léon Bloch and Eugène Bloch. However, I may be permitted to point out that the object of my work on the water-spark absorption spectrum of iron was to eliminate the more fundamental lines of the arc-spectrum of iron, and thus to elicit information

A New Method of Producing a Discharge in Hydrogen. 743

about the utility of this method as an aid to the classification of the spectra of more refractory elements, of which the absorption spectra cannot be readily studied by the usual method; I have pointed out that by modifying the experimental conditions, the “*d*” and “*F*¹” levels of the iron atom can be separated.

Yours faithfully,
A. K. SUR.

Allahabad.
8 April, 1926.

LXV. *A New Method of Producing a Discharge in Hydrogen.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN claiming in the July issue of your Magazine to describe a new method of producing a discharge in hydrogen, Messrs. E. W. B. Gill and R. H. Donaldson would appear to be unaware of earlier researches dealing with the production of discharges in gases at frequencies of the order 10^7 cycles per second*. In a recent communication to your Magazine, data have been given characterizing the discharge in hydrogen at the frequency 1.5×10^7 cycles per second†. These data indicated that the fields sustaining ionization by collision were considerably smaller than those necessary when using alternating potentials of commercial frequencies. Experiments were therefore commenced, and are now in progress, to determine the variation of dielectric strength of hydrogen and other gases with the frequency of the alternating potential applied to produce the discharge. It is anticipated that it will be possible soon to communicate the results which have been obtained.

Yours faithfully,

R. WINSTANLEY LUNT, M.Sc., Ph.D.

The William Ramsay Laboratories
of Physical and Inorganic Chemistry,
University College, London.
July 23, 1926.

* Lunt, Proc. Roy. Soc. A, cviii. p. 172 (1925).

† Lunt, Phil. Mag. xlix. p. 1238 (1925).

LXVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. i. p. 896.]

January 6th, 1926.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

THE following communication was read:—

‘The Geology of the Suk Hills (Kenya Colony).’ By Vincent G. Glenday, M.A., F.G.S., and John Parkinson, M.A., Sc.D., F.G.S.

The Suk Hills lie in the northern part of Kenya Colony, midway between Mount Elgon and the southern half of Lake Rudolf. Sekerr, their highest point, reaches an elevation of nearly 11,000 feet. So far as the authors are aware, this country hitherto has been geologically almost unknown. It is described by a southern traverse north of the Trans-Nzoia Escarpment to the Kerio River; and by a northern, including part of the Swam River and the Turkwal Gorge.

With insignificant exceptions, the rocks are of Eozoic age, and fall into two groups: a series of completely metamorphosed sediments, probably including ashes, and microcline-orthogneisses. As elsewhere, the former includes crystalline limestones, quartz-schists, kyanite-schists, garnet-mica-schists, and the like. After petrographical descriptions of the principal rock-types, the senior author concludes that the former group so closely resembles the Turoka Series from the border of Tanganyika Territory that they cannot be separated, the whole being contemporaneous in general terms. The strike of the planes of foliation of the Suk schists characteristically varies little from north and south. If the further conclusion is correct, that, of the two groups, the second is intrusive into the first, the relationship becomes of considerable importance, owing to the large area formed by these or closely similar rocks.

January 20th, 1926.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

The following communication was read:—

‘The Stratigraphy and Structure of the Cambrian Slate-Belt of Nantlle (Carnarvonshire).’ By Thomas Owen Morris, B.Sc., and Prof. William George Fearnside, M.A., F.G.S.

This paper describes the results obtained by mapping, on the 6-inch and 25-inch scales, the rocks and structures exposed over

about 10 square miles of the slate-quarrying district of Llanllyfni, Tal-y-sarn, Nantlle, and Moel Tryfan, in Carnarvonshire.

Stratigraphy.

The Nantlle Slate-Belt is the south-western part of the outcrop of the Cambrian rocks of Northern Carnarvonshire, which rest with appreciable unconformity upon the late pre-Cambrian volcanic rocks running south-westwards from Llanberis. The following succession has been established by the mapping, and is constant in all its divisions along the length and strike of the district:—

ORDOVICIAN.		Dark Slate Group; including some part of the zone of <i>Didymograptus murchisoni</i> .	
		Strike-Fault.	Thickness in feet.
UPPER CAMBRIAN.		Cymffyrch Grit Group; coarse grits with mudstone-beds	600
		Green Slate Group; green, greenish-blue, and light-brown slates, yielding <i>Hyolithus</i>	300
		Mottled Blue Slate Group; upper part: smooth silky-red slates; lower part: purple slates splashed with irregular green patches	600
		Pen-y-Bryn Grit Group; coarse massive grits.	200
MIDDLE CAMBRIAN.		Striped Blue Slate Group; stripes most abundant in the uppermost and in the lowest parts, which have a purplish tinge; stripes well-banded and generally fine-grained	600
		Dorothea Grit Group; coarse thickly-bedded grits, with intercalated thinly-bedded white and green banded silts	100
		Purple Slate Group; the upper part has a characteristic red portion, with abundant green spots; green stripes of coarse grit are most abundant in the highest and in a middle part of the group	800
LOWER CAMBRIAN.		Glog Grit Group; coarse grits, with intercalated beds of mudstone, quartzite, and conglomerate ...	2000
		Cilgwyn Conglomerate; conglomerate, with pebbles measuring up to 6 inches in length in a coarse grit-matrix	500
PRE- CAMBRIAN.		Tryfan Grit Group; upper part: finely banded green and white silt-rocks; lower part: coarse grits and felspathic tuffs	900
		Clogwyn Volcanic Group; rhyolitic and andesitic lavas and tuffs	1000

A correlation of these rocks with equivalent rocks in Southern Carnarvonshire and Merioneth is suggested. It is argued that

the Lower Cambrian sediments are land-waste from the pre-Cambrian rocks of North-Western Carnarvonshire and Anglesey, whereas the later Middle and Upper Cambrian material was brought in from an unknown source away to the east and south. Ordovician sediments are faulted against the basal member of the Upper Cambrian. A buttress of Ordovician volcanic rocks flanks the Nantlle area on the south-east side; but, within the area mapped, there are only altered dolerite-dykes, later than most of the impressed structures, to represent (and that a very late stage in) the cycle of Ordovician-Devonian igneous activity.

Structure.

The Nantlle district was deeply involved in the making of the Devonian alpine range, the basal wreck of which is now Snowdonia, and all sedimentary material within the Slate-Belt was compelled to fold, and then to crush until, both in bulk and in detail, it began to shear and creep. The importance of progressive movement in the development of cleavage is emphasized. Cleavage in the Nantlle Slate-Belt is almost vertical. Many folds have associated with them vertical strike-faults or slides, which, by tearing the middle limbs, have increased the vertical displacement. Often stronger beds are rolled out or packed as lenticles along surfaces of slip which behave as thrust-planes. Strong rocks rise on the north-western face of each slide, bend over, and are cut off by the next slide towards the north-west. The total displacement across individual slides, measured stratigraphically, may amount to many hundreds of feet. More boundaries of slate 'veins' and quarry properties are determined by slides than by bedding-planes. Between slides the slate-beds have characteristic anticlinal structures, the synclines being suppressed. Some slides are evident surfaces of discontinuity, but the movement along many slides was prior to the completion of growth of authigenic minerals, and, as along cleavage-planes, these surfaces of slip are sealed. The scale and frequency of the folding at Nantlle is comparable with that in the mining district of Wanlockhead. The slide-blocks are longer and narrower than the strike-fault strips between Caermarthen and St. Clears; but secondary thrusting is impersistent, and not as orderly as in the schuppen which affect the Cambrian rocks of the North-West Highlands.

With removal of load by denudation, joints and other tensional fractures have appeared. The direction of some of these is related to rock-texture, but bevels, etc. cross them at acute angles. The latest cross-faults are master-fractures, which traverse all other structures as also the pre- and post-Cambrian formations that flank the Slate-Belt. The direction of these is north of north-west, as the geometry of the half-dozen which cross the quarry-region suggests that block-movement was associated with north-

ward shift on the eastern side of each. Most of the dolerite-dykes follow bevels, and two have been intruded along the latest cross-faults.

A petrographic description of the pre-Cambrian rhyolites and of a hornblende-andesite is given, with chemical analyses. Petrographic evidence also establishes the existence of secondary (authigenic) micaceous minerals with or without recrystallized quartz in all the rocks of the Slate-Belt, and especially in those slates which are of greatest economic value. New-formed bladed chlorite is abundant in the Cambrian grits, and some of it is passing into biotite. Authigenic tourmaline in minute long prisms is a frequent constituent of both coarse and fine felspathic sediments throughout the Nantlle Slate-Belt.

February 3rd, 1926.--Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

Prof. S. JAMES SHAND, D.Sc., F.G.S., delivered a lecture on the *Alkaline Rocks and Ring-Intrusions of Pilansberg* (Transvaal), illustrated by specimens, diagrams, and lantern-slides.

He said that Pilansberg, a group of hills in the Western Transvaal, is the largest of the secondary eruptive complexes which are superimposed upon the great complex of the Bushveld. The energy which caused the extrusion of the Bushveld felsites, and the intrusion of the sheets of norite and red granite, was not quite exhausted by these tremendous events; but reactions went on underground, which led to the opening of new channels through which alkaline magma ascended. Plugs and dykes of syenite and foyaite cut the granite and the norite in Sekukuniland, in the Pretoria district (Franspoort, Leeuwfontein, etc.), and in the west, where Pilansberg presents one of the greatest intrusions of purely alkaline rocks in the world. The Berg is circular in outline, and covers about 200 square miles. The rocks may be grouped into (1) a volcanic series and (2) an intrusive series. The former includes felsites, phonolites, tinguaites, and a great development of tuff and breccia; these rocks formed a cover under which the intrusive series crystallized. The removal of most of the cover has laid bare the underlying foyaite and syenites, which are arranged in concentric rings, as follows:—(1) a core of pseudonepheline-syenite; (2) a ring of white granitic foyaite; (3) a ring of green porphyritic foyaite; (4) a half-ring of tinguaites; (5) another ring of white foyaite; and (6) a ring of red syenite. The principal problems presented by the Berg are the cause of this remarkable structure, and the origin and method of emplacement of the alkaline rocks.

February 19th, 1926.—Dr. John William Evans, C.B.E., F.R.S.,
President, in the Chair.

The PRESIDENT delivered his Anniversary Address dealing with the subject of Regions of Compression.

He said that the characteristic structures of regions of compression—that is to say: folding, thrust-faulting and slaty cleavage—are, as a rule, the result of horizontal forces ultimately to be attributed to the contraction of the Earth's interior as it cools. It has been doubted whether, with the energy released by radioactive elements, the Earth cools at all. It is certain, however, that the whole of that energy is not converted into heat; much must be employed in effecting physical, chemical, or atomic changes in the surrounding rock. The substance of the ionized pleochroic haloes in biotite-mica is hundreds of thousands of times greater than the radioactive material in the zircon round which they are formed, and they must represent a relatively enormous absorption of energy.

Dr. H. Jeffreys shows that the contraction on cooling of the crystallized rocks is more than enough to account for the folding of existing mountains. But there are many folds of ancient mountains, now worn down, which would require still more contraction. This may have occurred in the following ways: (1) the contraction of uncrystallized magma retaining the volatile constituents is greater than that of crystallized rocks; (2) the contraction on crystallization is equal to that on a fall of temperature of very many degrees; (3) contraction may take place on changes of crystal-structure, chemical composition, or even atomic nature; (4) contraction will result from the loss of volatile constituents; (5) it must also follow on the increase of pressure in the Earth's interior due to the slowing-down of its rotation. On the other hand, the extent of the crust may be locally increased in periods of tension by (1) infilling of rifts by igneous intrusions, and (2) slip-faulting; and also by hydration of rocks.

Compression and folding may also result (1) from change in the Earth's form on diminished rotation; (2) from change in the position of the crust relatively to (*a*) the poles and equator, (*b*) the maximum of gravitational force.

In illustration of the process of folding, two examples are described: (1) the 'Hercynian,' or 'Armorican,' folding of the south-western peninsula of England and South Wales; and (2) the Wealden folding between the Thames Valley and the 'Massif Central' of France. In the former case it is shown that the accumulations of sediments from mountains formed by Caledonian movements resulted in a 'sedimentation-subsidence.' This was slightly contracted and deepened by early Hercynian compression.

This 'compression-subsidence' allowed still greater accumulations of sediments. The oncoming of the main Hercynian compression contracted much more vigorously the basin of subsidence, forcing up the contained sediments into folds. The accumulated weight of these gave rise to a deep 'folding-subsidence.' A distinction is made between the exterior structure formed from the old floor of deposition and the interior structure consisting of the sediments deposited on it. The outflow of the plastic 'sima' from below the deepened basin raised its southern rim, with the result that in the course of the compression the folds were tilted northwards and dipped southwards. The folds are defined by the calcareous and arenaceous banding, while the argillaceous material between flowed rather than folded; and it is this flow which is now represented by slaty cleavage. In a later stage, both outer and inner structures were traversed by thrusts, which, like the folds and cleavage, dipped southwards. The greatest of these thrusts brought, in the extreme south, the pre-Cambrian rocks up against the Palæozoic. In the south of Devon and Cornwall this and other thrusts drove older rocks over new; but in North Devon new were brought over old. The displacement of the 'sima' in the course of mountain-building resulted in the intrusion of basic magmas, while the granites were probably derived from a reservoir beneath the uplifted pre-Cambrian rocks on the south.

The Wealden folding had its origin in sedimentary accumulations in a vast Triassic plain paved with the eroded outcrops of older rocks, and bordered by Hercynian highlands. The sedimentation-subsidence was widespread, and the compression in late Secondary and Tertiary times deepened it considerably, so that its floor has never been reached by borings south of the northern slope of the Wealden anticline, except in the neighbourhood of the Massif Central and the Hercynian tracts on the east and west. The actual compression in this region was small compared with that which occurred about the same time in the Pyrenees and in the Alps, but it threw the sediments of the interior structure into numerous folds.

A brief comparison was made between the great earth-movements of the Alps and those which formed the subject of the Address.

February 24th, 1926.—Dr. F. A. Bather, M.A., F.R.S.,
President, in the Chair.

The following communication was read:—

'The Geological Structure of Ben Lawers and Meall Corranaich (Perthshire).' By Gertrude Lilian Elles, M.B.E., D.Sc., F.G.S.

The country dealt with lies between Loch Tay on the south and Glen Lyon on the north, and between the Loch Tay Fault on the

east and the Ericht-Laidon-Tyndrum Fault on the west. Evidence is brought forward to show that the line of junction between the Ben Lui Schists and the Ben Lawers Schists is a mechanical one of the nature of a folded slide, the Ben Lawers Slide, the rocks above this slide constituting a veritable nappe, the Ben Lawers Nappe. The structure of the rocks composing this nappe is dealt with in some detail, and it is shown that the metamorphic condition of the rocks indicates that the folding now exhibited by them is a relatively late feature of the structural story, and obscures their original relationships, which seem to demand inversion of the beds on a large scale such as would be brought about by recumbent folding.

March 10th, 1926.—Dr. F. A. Bather, F.R.S., President.
in the Chair.

The following communication was read :—

‘The Pleistocene Deposits of the Lower Part of the Great Ouse Basin’. By Prof. John Edward Marr, Sc.D., F.R.S., For.Sec.G.S.

In a paper published in the Society’s Journal (vol. lxxv, 1919–20, p. 204) the author described the Pleistocene deposits in the immediate vicinity of Cambridge.

In the present paper a wider area is described. The results, in the main, confirm the conclusions of the previous paper.

It is argued that a period of aggradation in Lower Palæolithic times intervened between two periods of glaciation of the district, and that, subsequently to the second glaciation, erosion occurred, with minor periods of aggradation in Upper Palæolithic times.

The author also discusses the general character of the river-diversions which occurred in the district in Pleistocene times.

An Appendix by Mr. A. S. Kennard & Mr. B. B. Woodward deals with the non-marine mollusca.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

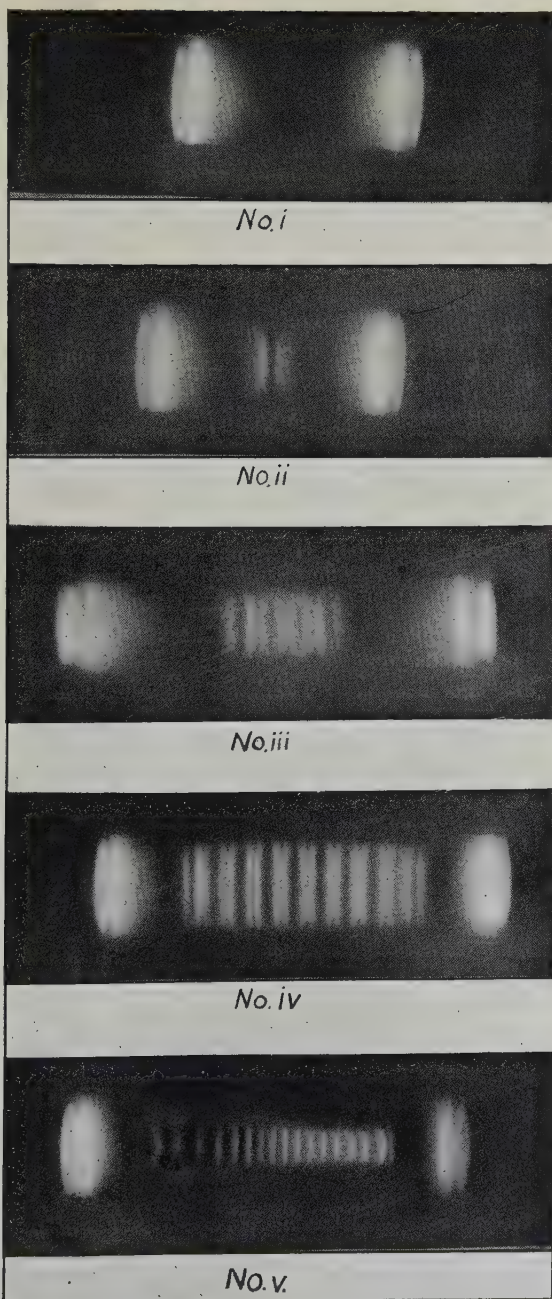




FIG. 1.

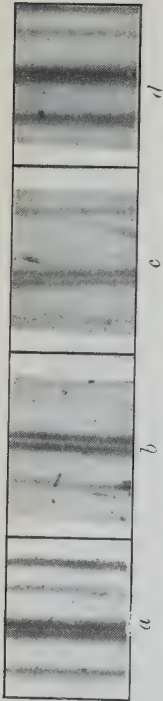


FIG. 2.

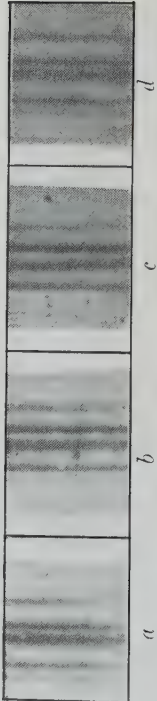


FIG. 3.

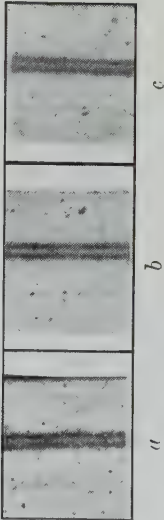


FIG. 4.



FIG. 5.

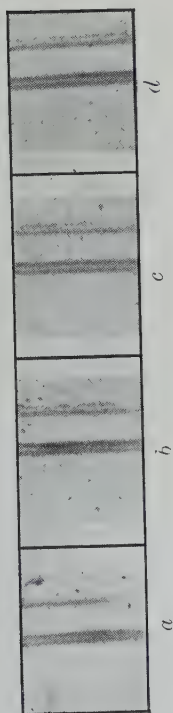


FIG. 6.

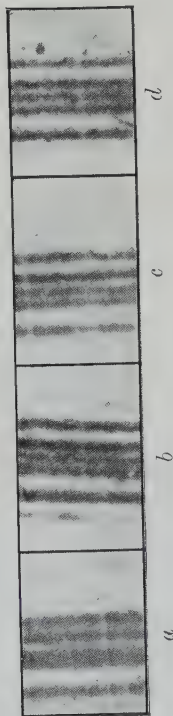


FIG. 7.

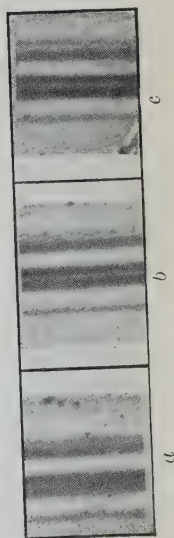


FIG. 8.

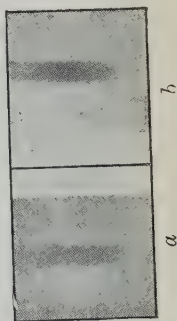
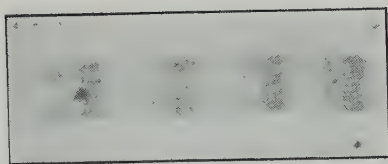
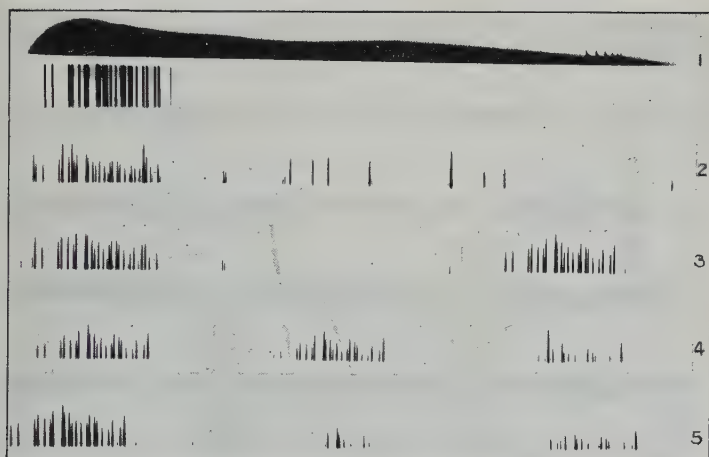


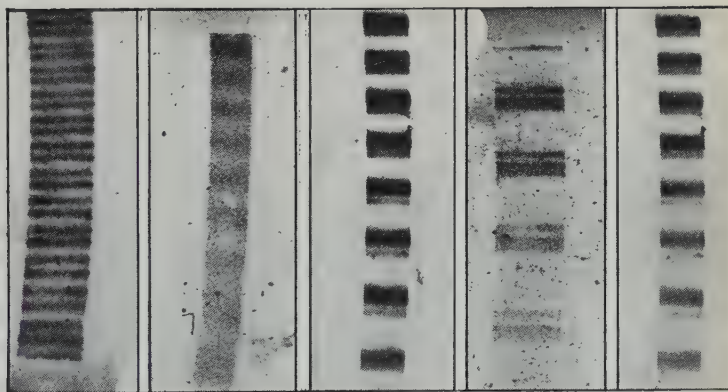
FIG. 9.











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